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### Catalytic Synthesis Of Sulfides Sulfoxides and Sulfones

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# CATALYTIC SYNTHESIS OF SULFIDES, SULFOXIDES AND SULFONES

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The present state of the synthesis of aliphatic sulfides, sulfoxides and sulfones in the presence of various catalysts is reviewed. Details of the formation of sulfides by interaction of  $H_2S$  with alcohols or alkenes, disproportionation of alkanethiols and of the synthesis of a cyclic sulfide, thiolane, from tetrahydrofuran and  $H_2S$  in the presence of acid-base catalysts, are discussed. Under consideration are the principles for the selection of catalysts, the effect of the reaction conditions on the direction of the transformations and the kinetics and mechanisms of the main and secondary processes. Data are given for the preparation of thiolane by reduction of thiophene with hydrogen in the presence of metals, metal complexes, and sulfide catalysts. Factors have been established which affect the activity and stability of these catalysts. A survey of studies of gas- and liquid-phase partial oxidation of aliphatic and cyclic sulfides with molecular oxygen is presented. Under consideration is also the contribution of substrate-catalyst complex formation to the catalyst activity in the formation of sulfoxides and sulfones. The mechanisms of reactions catalyzed by transition metal oxides and complexes and the factors for catalyst deactivation are discussed. Details of the catalytic hydrogenation of double bonds in unsaturated sulfoxides and sulfones are analyzed. Under comprehensive discussion is the hydrogenation of 2- and 3-thiolene 1,1-dioxides in the presence of various hydrogenation catalysts.

*Key words:* Alcohols, alkenes, catalysts, decomposition, dialkyl sulfides, ethers, hydrogenation, hydrogen sulfide, oxidation, sulfones, sulfoxides, thiolanes, thiols, thiophenes.

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## I. INTRODUCTION

Organic sulfides and their oxides have found practical application as solvents, extractants, biologically active substances and odorants as well as starting materials for the synthesis of various compounds.<sup>1-4</sup>

For preparative purposes aliphatic sulfides are most often obtained by the reaction of alkyl halides with sodium sulfides or thiolates. To synthesize thiacycloalkanes use is made of dihalo derivatives which are in turn obtained by multi-step syntheses. Sulfoxides and sulfones can be prepared via sulfide oxidation with various stoichiometric oxidants. In several cases the above methods prove to be inefficient since they require expensive or inaccessible raw materials. More appropriate are catalytic methods since they are highly efficient and applicable on a technical scale. For practical catalytic syntheses of sulfur compounds it is necessary to elaborate active and sulfur-resistant catalysts.

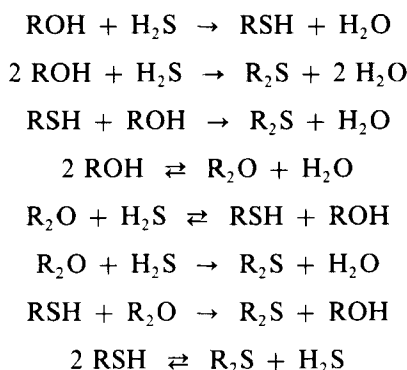
The scientific background for the choice of catalysts for reactions with sulfurorganic compounds involves concepts about intermediate chemical interactions between catalysts and reactants. The character of these interactions depends on the chemical properties of the catalysts and reactants.<sup>5</sup> These concepts concerning the mechanisms of the catalytic action are also useful for the discussion of the characteristic features of the reactions employed for obtaining sulfides and their oxides. In this review the present state of the art concerning the synthesis of aliphatic and cyclic sulfides, sulfoxides, and sulfones in the presence of various catalysts is presented.

## II. CATALYTIC SYNTHESIS OF SULFIDES

### II.1. Aliphatic Sulfides

*II.1.1. Synthesis of dialkyl sulfides from alcohols and H<sub>2</sub>S* An important method to obtain aliphatic sulfides is the interaction between alcohols and H<sub>2</sub>S. This reaction is

thermodynamically possible in a wide temperature range.<sup>6-9</sup> The process can involve the following reactions:

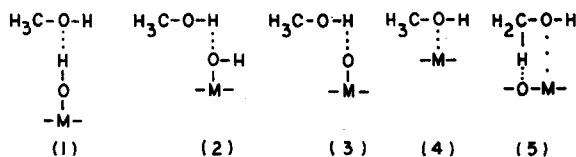


In the absence of catalysts the reaction rates are low. The process can be accelerated by amorphous silicates, zeolites, alumina unmodified or modified by mineral acids, and transition-metal oxides and sulfides. The reaction temperature is 200–450 °C. The rate of formation of sulfides increases with contact time and temperature. The selectivity for sulfide formation increases with decreasing H<sub>2</sub>S:alcohol ratio. The activity and selectivity are greatly dependent on the catalysts' acid-base characteristics.<sup>6-21</sup>

The most comprehensive study of the factors operative in the synthesis of sulfides has been carried out for the interaction of methanol with H<sub>2</sub>S.<sup>13-21</sup>

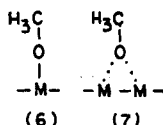
For a better understanding of the heterogeneous catalytic reaction mechanism it is necessary to acquire data concerning the adsorption of surface reactants on catalysts. Therefore the present state of studies on the adsorption of methanol and H<sub>2</sub>S and also their products—dimethyl ether, methanethiol, and dimethyl sulfide, will be considered here.

*II.1.1.1. Adsorption of reactants and products on catalysts* Methanol is adsorbed on the surface of solid catalysts to form various surface-bonded species. Hydrogen-bonded forms can be formed due to the interaction of acid hydroxyl groups of catalysts with the oxygen atom of methanol (1), interaction between the hydrogen atoms of hydroxyl groups of alcohols and surface basic OH groups (2), and to their interaction with structural oxygen (O<sup>2-</sup>) of a catalyst (3). Also possible is the formation of a coordinatively bonded alcohol structure with the participation of the catalyst cation and an oxygen atom of an alcohol (4) and sometimes additional bonds of a hydrogen atom to surface oxygen (basic OH groups or O<sup>2-</sup>)(5):

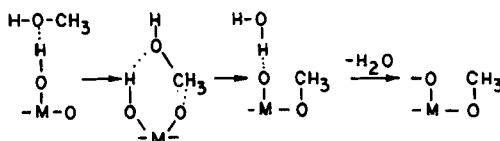


Structures 1–5 were found in methanol adsorption largely at temperatures below 150 °C and high surface coverage ( $\theta \geq 1$ ). At low  $\theta$  and temperatures above 150 °C the

associatively bonded methanol species decomposes and the surface is methoxylated (structures 6 and 7):

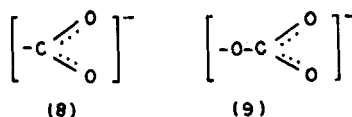


The methoxylation process is likely to occur as a concerted substitution with the participation of neighboring basic sites,<sup>22</sup> e.g.,



The process involving the participation of structures 2–4 is similar. Surface methoxy groups can interact with a second adsorbed methanol molecule, e.g. in the form of 2 and 3, to form dimethyl ether. This ether can also be obtained during interaction between 2 and 3.

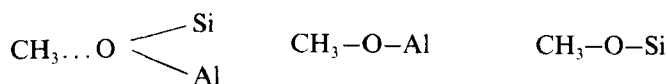
At high temperatures methanol adsorption on oxide catalysts leads to the formation of surface carboxylate (8) and carbonate (9) structures:



Experimental evidence for the existence of the various structures on catalysts was obtained in a great number of physico-chemical studies (IR spectroscopy, calorimetry, temperature-programmed desorption, NMR, and others).

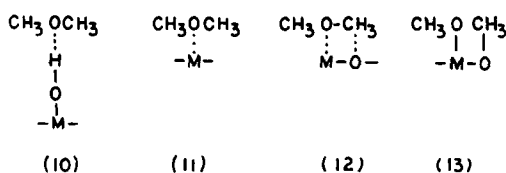
For example, the presence of structures 1–7 was established by analysis of changes in the IR spectra in the region of stretching vibrations of OH groups (3000–3600 cm<sup>-1</sup>) and stretching and deformational vibrations of CH<sub>3</sub>, C–H and C–O groups (2960–2820 and 1050–1090 cm<sup>-1</sup>). The presence of carboxylate and carbonate structures was confirmed by absorption near 1640–1350, 1260–1290, and 1020–1070 cm<sup>-1</sup>.

Hydrogen-bonded forms of methanol 1–5 have been found, in particular, for methanol adsorption on TiO<sub>2</sub>, MoO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>,<sup>23</sup> HY, NaY, NaX, HZSM-5 zeolites, and amorphous aluminosilicate. On the same catalysts and also on Al<sub>2</sub>O<sub>3</sub>, MgO, Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, NaOH/Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>/SiO<sub>2</sub> and TiO<sub>2</sub> + K<sup>23–31</sup> surfaces methoxy groups are formed. Carboxylate and carbonate structures have been observed on HZSM-5 and on Ti, Mo, Fe, and Cr oxides.<sup>23,25,28,32</sup> It has been established<sup>25</sup> that the surface of HZSM-5 contains various forms of methoxyl groups:



On dehydrated NaY zeolite methanol adsorption is observed (as evidenced by the appearance of absorption bands in the IR spectrum. The absorption bands, however, vanish after desorption at 200 °C. Weak adsorption of methanol was also observed on NaX where methanol is adsorbed with participation of a Na<sup>+</sup> ion.<sup>27,28</sup>

*Dimethyl ether* obtained from methanol is adsorbed on the surface to form various structures. Acid hydroxyl groups participate in the formation of the hydrogen-bonded ether structure **10**. On Lewis acid centers dimethyl ether forms a coordination bond (**11**) and also an additional bond (**12**) of a hydrogen atom of the CH<sub>3</sub> group with a basic center can be formed:

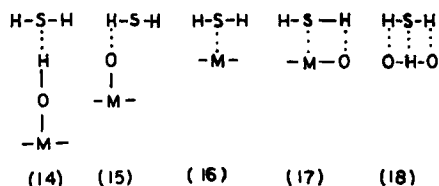


Structures **10–12** are mainly formed at low temperatures. As the temperature increases, they decompose to form surface methoxyl groups (**13**). Decomposition of structure **13** can lead to the formation of carboxylate and carbonate structures **8** and **9**.

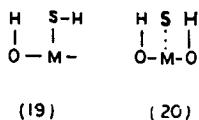
Associatively bound dimethyl ether structures were observed in IR spectroscopic studies of adsorption on high-silica zeolites<sup>29</sup> and Al<sub>2</sub>O<sub>3</sub><sup>32</sup> at 150–200 °C. Structures **12** and **13** are assumed to be formed after dimethyl ether adsorption on a sodium zeolite<sup>29</sup> and Al<sub>2</sub>O<sub>3</sub>,<sup>32</sup> respectively.

Thus, the same surface structures are produced by the adsorption of both dimethyl ether and methanol. At 200–450 °C similar conversion products of methanol and dimethyl ether are observed in the presence of η-Al<sub>2</sub>O<sub>3</sub>.<sup>33</sup>

*Hydrogen sulfide* is adsorbed on catalysts in various forms. Interaction of the sulfur atom with a proton center (**14**) and of a hydrogen atom of H<sub>2</sub>S with a basic center (**15**) can produce hydrogen-bonded structures. Lewis acid centers participate in the formation of a donor-acceptor complex (**16**) at acid-base regions of centers, i.e. structures **17–18**:



Associatively adsorbed H<sub>2</sub>S forms exist at relatively low temperatures and high surface coverage of H<sub>2</sub>S. With increasing temperature and diminishing extent of surface coverage, the dissociatively adsorbed H<sub>2</sub>S species **19** and **20** appear.



The most important evidence in favor of the formation of the above structures was obtained by IR spectroscopic studies. The IR spectrum of gaseous  $\text{H}_2\text{S}$  exhibits bands at 2611 and 2682  $\text{cm}^{-1}$ , due to stretching vibrations of SH groups, and a band at 1290  $\text{cm}^{-1}$  attributed to the deformational vibrations of H-S-H groups. During the adsorption of  $\text{H}_2\text{S}$  on catalysts the above bands shift towards 2560–2580 and 1334  $\text{cm}^{-1}$ , respectively. The simultaneous presence of these bands and their disappearance after heating of the catalyst at 100–200 °C is considered as evidence of the presence of undecomposed  $\text{H}_2\text{S}$  on the surface. The band due to HSH has low intensity and can be absent. Observation of only the S-H band is believed to be an argument for the presence of undecomposed  $\text{H}_2\text{S}$  only when accompanied by simultaneous changes in the region of hydroxyl group vibrations, i.e. an intensive decrease for the bands of basic OH groups (3780–3750  $\text{cm}^{-1}$ ) and increase for the bands “acid” OH groups (below 3600  $\text{cm}^{-1}$ ). The formation of structure **19** is evidenced by the disappearance of the bands of SH and “acid” OH groups during thermal desorption at 200–300 °C, whereas the surface sulfide (structure **20**) is not decomposed even upon heating at 500 °C. Extensive decomposition of  $\text{H}_2\text{S}$  (structure **20**) is evidenced by the high intensity of absorption in the region of “acid” OH group vibrations, the presence of bands belonging to adsorbed water (1600  $\text{cm}^{-1}$ ), the data of catalyst analysis for the sulfur concentration before and after  $\text{H}_2\text{S}$  adsorption at elevated temperatures and also the measured concentrations of catalyst active sites. The available data on  $\text{H}_2\text{S}$  adsorption on specific catalysts<sup>34–55</sup> are considered below.

$\text{H}_2\text{S}$  adsorption on  $\text{SiO}_2$  involves the participation of “acid” Si-OH groups forming a weak hydrogen bond with a sulfur atom (structure **14**).<sup>35,37,42</sup> The same structure is formed during  $\text{H}_2\text{S}$  adsorption at 20–200 °C on the  $\text{H}_3\text{PO}_4/\text{SiO}_2$  sample with stronger proton-donor centers with the participation of P-OH groups. At different surface coverages the IR spectra exhibit bands typical for undecomposed  $\text{H}_2\text{S}$  and the shifted band of P-OH groups. Pyridine adsorption data indicate that in this case the proton-donor centers are completely blocked. Vacuum treatment of this sample at 200 °C leads to the disappearance of the bands belonging to adsorbed  $\text{H}_2\text{S}$  and to the complete liberation of proton centers.<sup>38</sup> These results have been confirmed by high-resolution solid-state  $^1\text{H}$  NMR studies of  $\text{H}_2\text{S}$  adsorption.<sup>34,36</sup> It was established that at different surface coverages the spectrum exhibits only lines with  $\delta = 0.8$  ppm, which indicates associative adsorption of  $\text{H}_2\text{S}$ . In a similar way  $\text{H}_2\text{S}$  adsorption takes place on amorphous aluminosilicate and HNaY and HZSM zeolites<sup>37,39</sup> containing a large number of surface proton centers. Moreover, these catalysts contain strong Lewis acid and moderately basic centers. At low temperatures and high surface coverages by  $\text{H}_2\text{S}$  Lewis acid centers take part in the formation of structure **16** of adsorbed  $\text{H}_2\text{S}$ . On paired centers structure **17** is formed. At low surfaces coverages  $\text{H}_2\text{S}$  mainly dissociates to SH and OH groups (structure **19**). NMR studies indicate<sup>34</sup> that at low surface coverages dissociative chemisorption of  $\text{H}_2\text{S}$  takes place since there appears a signal with a chemical shift  $\delta = -1.6$  ppm, attributed to the  $\text{SH}^-$  species bound to a coordinatively unsaturated Al atom. At high coverages adsorption takes place without  $\text{H}_2\text{S}$  dissociation.

On  $K_2CO_3/SiO_2$  containing strongly basic and weak Lewis acid centers ( $K^+$  cations)  $H_2S$  adsorption at 20–200 °C leads to decomposition with the dissociation of one or two S–H bonds (structures **19** and **20**). IR spectroscopic studies of deuteriochloroform adsorption showed<sup>38</sup> that the process is accompanied by the blocking of basic centers. The NMR spectrum of the sample with adsorbed  $H_2S$  exhibits a signal with  $\delta = -3.5$  ppm belonging to an SH species bound to an alkali metal ion. At high surface coverage of this sample by  $H_2S$  there exist forms of undecomposed  $H_2S$ .

On an NaX zeolite at 20–120 °C and low surface coverage the extent of  $H_2S$  dissociation to  $S^{2-}$  and  $2H^+$  (structure **20**) with the participation of strong Lewis centers is very small.  $H_2S$  largely decomposes at one S–H bond to form acid OH groups and SH species bound to  $Na^+$ .<sup>37,41,48,49</sup> NMR studies revealed SH species bound to  $Na^+$  ( $\delta = 3.7$  ppm). NaY also contain these structures, but only to a very small extent.<sup>34</sup> On NaY, CaY and MgY the dissociation largely takes place at both H–S–H bonds (structure **20**).<sup>39</sup> In accordance with the IR spectroscopic data it was suggested that on Y-zeolites with Cd, Cu, Ni, Ag and Co cations and on amorphous aluminosilicates modified with Cu and Ag ions cations take part in the formation of a metal ion–SH bond; protons interact with oxygen anions of the zeolite crystal lattice to form acid hydroxyl groups and a small amount of surface sulfides. Different chemisorption mechanisms of  $H_2S$  on the above catalysts and NaY, MgY, and CaY zeolites are interpreted in terms of the concepts of hard and soft acids and basis (HSAB). Cd, Cu, Ni, Ag and Co cations are soft to moderate acids; they possess increased affinity towards  $H_2S$  which is a soft base. At the same time the interaction of hard acids (Na, Ca, and Mg) with  $H_2S$  is disfavored.<sup>39</sup>

On  $Al_2O_3$   $H_2S$  is adsorbed in various forms. According to the IR spectroscopic data it can be suggested that at high surface coverages  $H_2S$  adsorption takes place without decomposition to form structures **14** and **15**.<sup>44</sup> Associatively adsorbed forms of  $H_2S$  have also been found.<sup>50–53</sup> In the NMR spectra these structures give rise to signals with  $\delta = 1.2$ – $1.8$  ppm.<sup>34</sup> A thermodesorption curve obtained by heating the sample with adsorbed  $H_2S$  at 200 °C has a maximum peak near 127 °C, belonging to structure **16**.<sup>37</sup> After heating of an  $Al_2O_3$  sample with adsorbed  $H_2S$  on its surface, a maximum peak is observed near 287 °C and attributed to  $H_2S$  dissociatively chemisorbed with the participation of Lewis acid and basic centers (structure **19**). The amount of  $H_2S$  decomposed on the surface is approximately the same as that of its associatively bound form.<sup>37</sup> Al–SH structures were identified in the NMR spectra as responsible for signals at  $\delta = -1.6$  ÷  $-2.0$  ppm.<sup>34</sup>

It has been established from the IR spectra of adsorbed CO and  $CDCl_3$ <sup>44</sup> that vacuum treatment of  $Al_2O_3$  with adsorbed  $H_2S$  on its surface at 200 °C leads only to partial liberation of basic and Lewis acid centers and, apparently, surface structures of the type Al–S are formed. Temperature increase to 450–500 °C leads to almost complete removal of strongly bound  $H_2S$ .<sup>37</sup>

Upon introduction of 0.3–4.0 wt.%  $Na^+$ ,  $Mg^{2+}$ , and  $Zn^{2+}$  into  $Al_2O_3$  the total amount of adsorbed  $H_2S$  per unit surface increases since cation insertion into the  $Al_2O_3$  lattice to form a surface spinel increases the number of surface adsorption sites.<sup>37</sup> The ratio between the associative and the dissociative adsorption forms of  $H_2S$  on the modified surface is practically the same as for  $Al_2O_3$ . But since in the modified samples the Lewis acid centers are weakened, the temperature peak referring to dissociatively chemisorbed  $H_2S$  shifts by 40–60 °C. IR spectroscopic studies<sup>34</sup> indicate that with an

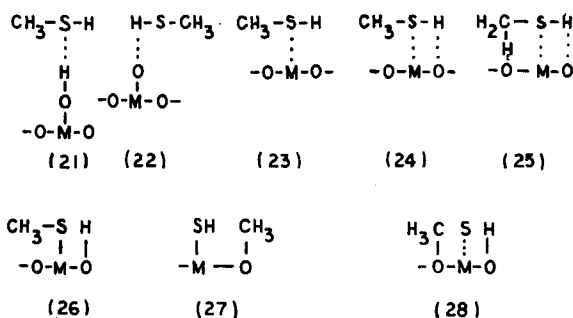


increase of  $[\text{Na}^+]$  from 1 to 4.5 wt.% the intensity of the bands from SH groups increase, thus confirming the existence of  $\text{Na}^+ - \text{SH}$  bonds. The total amount of adsorbed  $\text{H}_2\text{S}$  increases.

Introduction of additives decreasing the concentration and strength of basic centers ( $\text{HF}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{MoO}_3$ ) into  $\text{Al}_2\text{O}_3$  reduces the adsorption capacity of the sample and the content of dissociatively chemisorbed  $\text{H}_2\text{S}$ . With high concentration of  $\text{MoO}_3$  on  $\text{Al}_2\text{O}_3$  the amount of structures of type **20** increases.<sup>37</sup>

On  $\text{TiO}_2$  just like on  $\text{Al}_2\text{O}_3$ , both dissociative adsorption of  $\text{H}_2\text{S}$  to form thiolate structures and reversible adsorption without decomposition take place.<sup>55</sup>

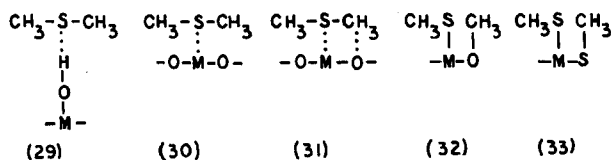
*Methanethiol* is adsorbed on the catalyst like  $\text{H}_2\text{S}$  and generates the following structures:



Associative adsorption has been observed on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  at large surface coverages by  $\text{H}_2\text{S}$ <sup>35,50,53,56</sup> and  $\text{TiO}_2$ .<sup>55</sup> It is suggested that a hydrogen bond between the sulfur atom of methanethiol and surface hydroxyl groups is formed (structure **21**).<sup>50,53</sup> It was noted<sup>35,56</sup> that in this case the S-H bond strength is higher for methanethiol than for  $\text{H}_2\text{S}$ .

At small surface coverages on  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  methanethiol is dissociatively adsorbed<sup>50,55</sup> due to its coordination to  $\text{Al}^{3+}$  or  $\text{Ti}^{4+}$  structures **23–25** decompose to structure **26**. IR spectroscopic data show bands typical for  $\text{CH}_3\text{S}$  and OH groups, and this process occurs with the participation of moderately strong Lewis acid centers.<sup>50</sup> On strong acid centers of  $\text{Al}_2\text{O}_3$  extensive methanethiol decomposition takes place to produce Al-S. In the course of methanethiol adsorption on  $\text{Al}_2\text{O}_3$  dimethyl sulfide and  $\text{H}_2\text{S}$  evolve into the gas phase and their yield rises from 7 to 50% when the temperature is increased from 35 to 100 °C.<sup>50</sup>

*Dimethyl sulfide* is adsorbed on the surface with the participation of various centers. Under the effect of acid hydroxyl groups it is protonated on the sulfur atom (structure **29**), with Lewis acid centers a donor-acceptor complex **30** is formed. Also possible is an additional bond between the  $\text{CH}_3$  groups and a basic center (structure **31**):



**Table 1.** Thermodesorption of dimethyl sulfide adsorbed on metal oxides at various temperatures<sup>5</sup>

| Adsorption temperature of dimethyl sulfide (°C) | Relative yield of thermodesorption products |                  |                               |                                |                  |                               |
|---|---|------------------|-------------------------------|--------------------------------|------------------|-------------------------------|
|   | Dimethyl sulfide                            |                  |                               | Gaseous decomposition products |                  |                               |
|   | Al <sub>2</sub> O <sub>3</sub>              | MoO <sub>3</sub> | V <sub>2</sub> O <sub>5</sub> | Al <sub>2</sub> O <sub>3</sub> | MoO <sub>3</sub> | V <sub>2</sub> O <sub>5</sub> |
| 70  | 90  | 70               | 50                            | 16                             | 8                | 6                             |
| 100   | 80  | 60               | 40                            | 17                             | 9                | 8                             |
| 150   | 50  | 40               | 5                             | 18                             | 11               | 10                            |
| 200   | 20  | 10               | 0                             | 19                             | 14               | 12                            |
| 250   | 0   | 0                | 0                             | 22                             | 17               | 16                            |

Structures **29–31** exist at temperatures below 100–200 °C. At elevated temperatures and small surface coverages dimethyl sulfide decomposes with cleavage of the C–S bond to form CH<sub>3</sub>S and CH<sub>3</sub>O groups.<sup>32,33</sup> On metal sulfides only CH<sub>3</sub>S structures (**33**) can form.

The existence of structure **29** has been confirmed by studies of dimethyl sulfide adsorption on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub><sup>35,56</sup> and TiO<sub>2</sub>.<sup>55</sup> Arguments in favor of the formation of dimethyl sulfide coordinatively bonded to the surface through a sulfur atom (structures **30** and **31**) have been obtained for Al, Cr, Ti, Mo, Mn, and V oxides.<sup>50,55–59</sup> On these oxides dissociative adsorption of dimethyl sulfide to structures **32** and **33** also takes place.<sup>55,58,59</sup> The higher the adsorption temperature of dimethyl sulfide on these oxides, the lower the amount of intact sulfide produced under thermodesorption and the higher the content of decomposition products. At temperatures above 200 °C the surface of these catalysts contains no intact dimethyl sulfide structures<sup>5</sup> (Table 1).

### II.1.1.2. Catalytic Reaction of Methanol with H<sub>2</sub>S

Methanol interaction with H<sub>2</sub>S has been studied in detail<sup>13–21</sup> in the presence of catalysts with different acid-base properties.

The acid and basic centers on the catalysts were identified by means of the IR spectra of the adsorbed test compounds. Pyridine or ammonia, CO and pyridine, and deuteriochloroform, respectively, were used as test compounds for proton, Lewis acid and basic centers, respectively. The concentration of these centers *C* (in μmol/g or m<sup>2</sup>) was determined by measurement of the ratio of the integral intensity of the bands of the adsorbed test compounds to the integral absorption coefficient. The strength of proton-donor centers was deduced from the proton affinity towards CO (PA (kJ/mol)), that of Lewis acid centers was characterized by the reaction enthalpy for their interaction with CO determined from the displacement of the bands for CO adsorbed at low temperature (Q<sub>CO</sub> (kJ/mol)). The strength of the basic centers was characterized on a PA scale (kJ/mol) according to the IR band shift of the CDCl<sub>3</sub> hydrogen-bonded to basic surface centers. The acid-base characteristics of a number of catalysts are given in Table 2, cf. also.<sup>13,15,16</sup>

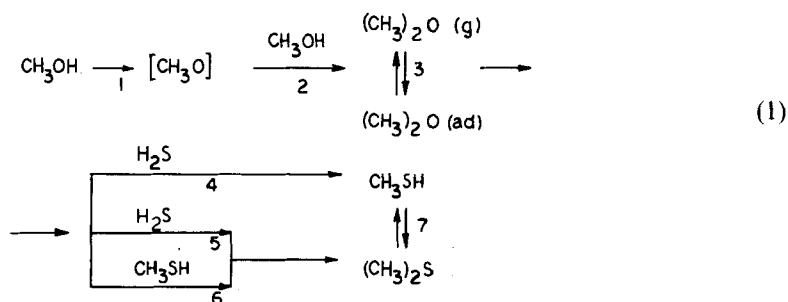
The main products of methanol interaction with H<sub>2</sub>S in the presence of all studied catalysts are methanethiol, dimethyl sulfide, dimethyl ether, and water. Under certain conditions small amounts of decomposition products, i.e. CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>, are formed.

**Table 2.** Acid-base properties of catalysts<sup>13,15,16</sup>

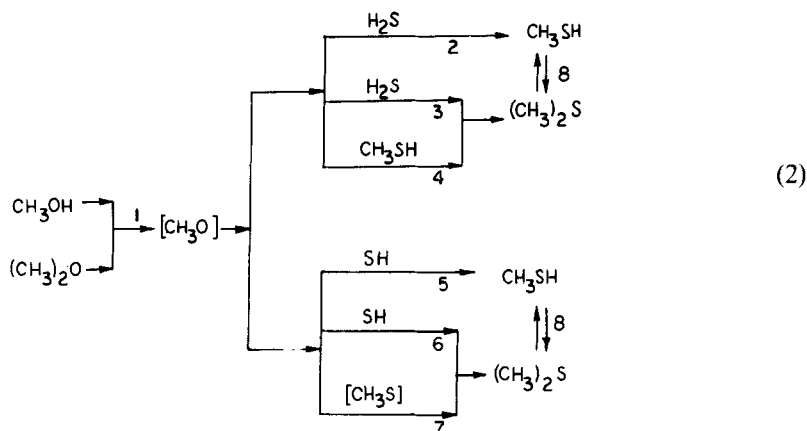
| Catalyst  | Proton centers                 |                                    | Lewis acid centers             |                                    | Basic centers                  |                                    |
|---|--------------------------------|------------------------------------|--------------------------------|------------------------------------|--------------------------------|------------------------------------|
|   | PA                             | C                                  | Q <sub>CO</sub>                | C                                  | PA <sup>B</sup>                | C                                  |
|   | $\frac{\text{kJ}}{\text{mol}}$ | $\frac{\mu\text{mol}}{\text{m}^2}$ | $\frac{\text{kJ}}{\text{mol}}$ | $\frac{\mu\text{mol}}{\text{m}^2}$ | $\frac{\text{kJ}}{\text{mol}}$ | $\frac{\mu\text{mol}}{\text{m}^2}$ |
| SiO <sub>2</sub>  | 1390                           | 2.8                                | —                              | 0                                  | —                              | 0                                  |
| 30% H <sub>3</sub> PO <sub>4</sub> /SiO <sub>2</sub>                    | ~1300                          | 0.6                                | —                              | 0                                  | —                              | 0                                  |
| HNaY  | 1180                           | 0.15                               | 54                             | 0.1                                | 800-900                        | 1.9                                |
| NaY   | —                              | 0                                  | 20                             | 3.6                                |                                |                                    |
| HZSM-5<br>(Si/Al = 60)  | 1180                           | 0.45                               | 42                             | 0.1                                |                                |                                    |
| $\gamma$ -Al <sub>2</sub> O <sub>3</sub>                                | 1410                           | 0                                  | 34                             | 2.3                                | 800-900                        | 4.0                                |
| 3% HF/Al <sub>2</sub> O <sub>3</sub>                                    | <1300                          | 0.25                               | 42                             | 2.0                                | <800                           | 2.4                                |
| 2.3% Cr <sub>2</sub> O <sub>3</sub> /<br>Al <sub>2</sub> O <sub>3</sub> | <1300                          | 0.15                               | 36                             | 2.4                                | 900                            | 2.8                                |
| 3.5% NaOH/<br>Al <sub>2</sub> O <sub>3</sub>                            | —                              | 0                                  | 26                             | 1.0                                | 830                            | 2.3                                |
|   |                                |                                    |                                |                                    | 930                            | 0.6                                |
|   |                                |                                    |                                |                                    | 960                            | 1.0                                |
| 10% Na <sub>2</sub> WO <sub>4</sub> /<br>Al <sub>2</sub> O <sub>3</sub> | —                              | 0                                  | 32                             | 1.1                                | 800                            | 2.4                                |
|   |                                |                                    |                                |                                    | 900                            | 0.6                                |
|   |                                |                                    |                                |                                    | 930                            | 0.5                                |
| 10% K <sub>2</sub> CO <sub>3</sub> /SiO <sub>2</sub>                    | —                              | 0                                  | —                              | 0                                  | 925-970                        | 2.1                                |
| MgO   | —                              | 0                                  | 16                             | 3.9                                |                                |                                    |

\* accurate to  $\pm 20$  kJ/mol.

One of the ways for methanethiol and dimethyl sulfide formation is the interaction of dimethyl ether formed from methanol and H<sub>2</sub>S:



But like methanol, dimethyl ether is dissociatively chemisorbed on the catalyst to form CH<sub>3</sub>O groups and under steady-state conditions the catalyst surface is methoxylated. More probable is the formation of methanethiol and dimethyl sulfide with the participation of methoxy groups rather than dimethyl ether.



The acid-base characteristics of the catalysts are responsible for the predominance of a specific reaction route.

Studies of methanol reaction with  $\text{H}_2\text{S}$  catalyzed by NaX, NaY, NaZSM-5, HNaY, and HZSM-5 zeolites at 350–400 °C show that these catalysts differ in their activity towards methanethiol and dimethyl sulfide.<sup>18–21</sup> Comparison of these catalysts with respect to product yields obtained at constant contact times and extensive, sometimes complete, methanol conversion, did not permit to establish a scale of relative activities of zeolites.<sup>18,19</sup> A quantitative comparison of the activities of various zeolites was performed with the kinetic data of.<sup>21</sup> The experiments were carried out at atmospheric pressure in the kinetic region, methanol concentrations  $C = 17$  and  $28$  mmol/h and with substoichiometric and excess ratios of  $\text{H}_2\text{S}$  to methanol (molar ratio  $\text{H}_2\text{S}:\text{CH}_3\text{OH} = 0.6$  and  $1.6$ ). In the presence of each catalyst the dependence of methanol conversion, product yields and selectivity on the contact time,  $\tau$ , ( $\tau = V_c/V_g$ , where  $V_c$  is the catalyst volume (ml) and  $V_g$  is the total gas flow rate (ml/s)) was determined. A measure for the catalyst activity was the rate of the total methanol decomposition or its conversion to reaction products per 1 g or  $1 \text{ m}^2$  catalyst  $W$  (mmol/h) at the same methanol conversion  $X$  (%) for various catalysts. The selectivity (%) is measured as the ratio of product yield to methanol conversion.

In the presence of HZSM-5, HNaY, NaX, and NaY zeolites variations in methanol conversion and the product yields were determined at  $T = 260$ – $420$  °C, contact time 0.1–20 s. The methanol conversion was in the range 4–100%.

At constant temperatures and initial reactant concentrations in the presence of all the zeolites the conversion and the yield of dimethyl sulfide rise with increasing contact time. The methanol yield rises to a certain limit, then it slightly decreases, that of dimethyl ether falls (Table 3). On NaX and NaY zeolites the methanethiol yield is higher at all contact times than that of dimethyl sulfide, particularly with excess  $\text{H}_2\text{S}$ . On HNaY and HZSM\* with substoichiometric and excess  $\text{H}_2\text{S}$ , the yield of dimethyl sulfide is considerably higher than that of methanethiol. With increasing methanol conversion, up to approximately 60%, the selectivity towards thiol and sulfide on all zeolites is constant.

\*HZSM zeolite type HZSM-5.

**Table 3.** The effect of the contact time on methanol conversion and on the selectivity towards the reaction products,  $T = 360^\circ\text{C}^{21}$ 

| Zeolite | X (%) | $\tau$ (s) | Selectivity (%) at $\text{H}_2\text{S}:\text{CH}_3\text{OH} = 0.6$ |                           |                           | $\tau$ (s) | Selectivity (%) at $\text{H}_2\text{S}:\text{CH}_3\text{OH} = 1.6$ |                           |                           |
|---------|-------|------------|--|---------------------------|---------------------------|------------|--|---------------------------|---------------------------|
|         |       |            | $\text{CH}_3\text{SH}$   | $(\text{CH}_3)_2\text{S}$ | $(\text{CH}_3)_2\text{O}$ |            | $\text{CH}_3\text{SH}$   | $(\text{CH}_3)_2\text{S}$ | $(\text{CH}_3)_2\text{O}$ |
| NaX     | 20    | 1.0        | 60   | 34                        | 6                         | 0.2        | 90   | 10                        | 0                         |
|         | 40    | 2.5        | 60   | 35                        | 5                         | 0.7        | 90   | 10                        | 0                         |
|         | 60    | 4.5        | 60   | 37                        | 3                         | 1.6        | 88   | 12                        | 0                         |
|         | 80    | 7.5        | 56   | 44                        | 0                         | 4.0        | 83   | 17                        | 0                         |
| NaY     | 40    | 16         | 62   | 32                        | 6                         | 3.5        | 80   | 20                        | 0                         |
|         | 60    | 30         | 63   | 37                        | 0                         | 5.5        | 77   | 23                        | 0                         |
|         | 80    | 45         | 58   | 42                        | 0                         | —          | —  | —                         | —                         |
| HNaY    | 40    | 1.0        | 8  | 30                        | 62                        | 0.5        | 15   | 37                        | 48                        |
|         | 60    | 2.5        | 10   | 33                        | 57                        | 0.75       | 17   | 38                        | 45                        |
|         | 80    | 7.5        | 14   | 55                        | 31                        | 1.2        | 19   | 40                        | 41                        |
|         | 90    | 15         | 5  | 78                        | 17                        | 1.7        | 17   | 46                        | 37                        |
| HZSM    | 40    | 0.36       | 10   | 85                        | 5                         | 0.13       | 15   | 85                        | 0                         |
|         | 60    | 0.6        | 10   | 87                        | 3                         | 0.2        | 18   | 82                        | 0                         |
|         | 80    | 0.9        | 6  | 91                        | 0                         | 0.3        | 19   | 81                        | 0                         |
|         | 90    | 1.1        | 11   | 89                        | 0                         | 0.4        | 20   | 80                        | 0                         |

At higher conversion degrees, the selectivity towards dimethyl sulfide increases slightly and that towards methanethiol decreases (Table 3).

It can be concluded that methanethiol and dimethyl sulfide are the main products obtained from methanol and that their formation follows independent routes. At high methanol conversion the thiol formed can undergo further conversions, e.g., following the reactions given on p. 281. The kinetic data, however, suggest that the contributions of these reactions producing dimethyl sulfide are small on all zeolites examined.

With increasing methanol conversion the selectivity towards dimethyl ether decreases. On all zeolites, except HNaY, at  $X = 20\text{--}60\%$  it is lower than towards the thiol and the sulfide. The decrease of the selectivity towards the ether with increasing conversion can be due to its consumption along routs 4–6 in Scheme 1 with the formation of dimethyl sulfide and methanethiol and also partly to the decrease in the concentration of surface  $\text{CH}_3\text{O}$  groups interacting with  $\text{H}_2\text{S}$  or of  $\text{SH}^-$ ,  $\text{CH}_3\text{SH}$  and  $\text{CH}_3\text{S}^-$  (Scheme 2), since in this case the reaction rate of methoxyl groups with methanol decreases.

An increase of the ratio  $\text{H}_2\text{S}:\text{CH}_3\text{OH}$  from 0.6 to 1.6 in the presence of all zeolites examined increases the total rate of methanol conversion, e.g. at  $X = 40\text{--}60\%$  the total rate grows 2–5 times. In this case the selectivity towards methanethiol grows 1.5–2 times, that towards dimethyl sulfide on HNaY and HZSM rises 1.2 times, whereas on NaX and NaY it decreases by a factor of 2.5–3.5. The selectivity towards dimethyl ether decreases with increasing ratio  $\text{H}_2\text{S}:\text{CH}_3\text{OH}$ .

The reaction rate increases with rising temperature. For example, some results obtained on HZSM-5 with  $\text{Si}/\text{Al} = 45$  are given in Table 4. As can be seen over the total range of temperatures and contact times the yield of dimethyl sulfide and the corresponding selectivity are much higher than those for methanethiol. At all temperatures the selectivity towards dimethyl ether ( $\eta_e$ ) is considerably high only at low methanol conversions. For example, at  $X \leq 5\%$  we have  $\eta_e = 80\text{--}90\%$  and at  $X = 10\text{--}30$  and  $100\%$ ,  $\eta_e = 20\text{--}40$  and  $0\%$ , respectively.

**Table 4.** Interaction of methanol with H<sub>2</sub>S at various temperatures and contact times in the presence of HZSM zeolite (H<sub>2</sub>S:CH<sub>3</sub>OH = 0.6)<sup>21</sup>

| T (°C) | τ (s) | CH <sub>3</sub> OH<br>conver-<br>sion (%) | Yield (mol.%)      |                                   |                                   |
|--------|-------|---|--------------------|-----------------------------------|-----------------------------------|
|        |       |   | CH <sub>3</sub> SH | (CH <sub>3</sub> ) <sub>2</sub> S | (CH <sub>3</sub> ) <sub>2</sub> O |
| 260    | 1.2   | 9   | < 0.1              | 4                                 | 5                                 |
|        | 3.0   | 18  | 0.2                | 12                                | 6                                 |
| 280    | 1.2   | 12  | 0.2                | 6                                 | 6                                 |
|        | 2.2   | 21  | 1.0                | 15                                | 5                                 |
| 300    | 0.12  | 4   | < 0.1              | 0.3                               | 3.6                               |
|        | 0.4   | 9   | < 0.1              | 5                                 | 4                                 |
| 360    | 1.2   | 28  | 1                  | 20                                | 7                                 |
|        | 0.2   | 20  | 2                  | 15                                | 3                                 |
| 400    | 1.0   | 87  | 2                  | 85                                | 0                                 |
|        | 0.02  | 6   | 0                  | 3                                 | 4                                 |
|        | 0.04  | 14  | 0.2                | 10                                | 4                                 |
|        | 0.12  | 32  | 2                  | 20                                | 10                                |
| 420    | 1.2   | 100                                       | 10                 | 88                                | 2                                 |
|        | 0.02  | 8   | 0                  | 4                                 | 4                                 |
|        | 0.04  | 17  | 0.2                | 11                                | 6                                 |

With rising temperature one can observe an increase in the total rate of methanol formation, and the formation rates of methanethiol and dimethyl sulfide, but the formation rate of dimethyl ether drops. The selectivity towards the thiol and the sulfide grows and that towards the ether falls. A linear logarithmic dependence of the constant reaction rate (at X = 20%) on 1/T can be seen. The apparent activation energy is  $79 \pm 4$  kJ/mol,  $\lg K_0 = 9.03$ .

A comparison of the activities and selectivities for zeolites was made at the same methanol conversion, e.g. X = 50% (Table 5). As can be seen, the catalytic properties of zeolites depend on their composition and hence the acid-base characteristics of their surfaces.

The surface of the decationated HZSM zeolites examined contains a great number

**Table 5.** Catalyst activities in the reaction of CH<sub>3</sub>OH with H<sub>2</sub>S, T = 360 °C, X<sub>methanol</sub> = 50%<sup>21</sup>

| Catalyst          | Rate (μmol/g·h)                 |                    | Selectivity (%)                   |                                   |
|-------------------|---------------------------------|--------------------|-----------------------------------|-----------------------------------|
|                   | CH <sub>3</sub> OH              | CH <sub>3</sub> SH | (CH <sub>3</sub> ) <sub>2</sub> S | (CH <sub>3</sub> ) <sub>2</sub> O |
|                   | [H <sub>2</sub> S] = 17 mmol/l, |                    | [CH <sub>3</sub> OH] = 28 mmol/l  |                                   |
| NaX               | 27.0                            | 16.2               | 10.3                              | 0.5                               |
| NaY               | 3.0                             | 1.8                | 1.1                               | 0.1                               |
| HNaY              | 61.0                            | 4.9                | 19.5                              | 36.6                              |
| HZSM <sup>a</sup> | 175                             | 8.5                | 150                               | 6.5                               |
| HZSM <sup>b</sup> | 115                             | 4.8                | 72                                | 43                                |
| HZSM <sup>c</sup> | 100                             | 2.0                | 58                                | 40                                |
|                   | [H <sub>2</sub> S] = 28 mmol/l, |                    | [CH <sub>3</sub> OH] = 17 mmol/l  |                                   |
| NaX               | 52.4                            | 46.1               | 6.3                               | 0                                 |
| NaY               | 7.1                             | 5.4                | 1.7                               | 0                                 |
| HNaY              | 92.4                            | 14.7               | 33.2                              | 44.2                              |
| HZSM <sup>a</sup> | 280                             | 56.0               | 224                               | 0                                 |

<sup>a,b,c</sup> SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 45, 100, and 500, respectively.

(100–300  $\mu\text{mol/g}$ ) of proton centers with  $\text{PA}^{\text{a}} \sim 1200 \text{ kJ/mol}$ , one-two orders of magnitude less strong Lewis acid centers,  $\text{Al}^{3+}$  cations localized outside the lattice and some basic centers, oxygen anions of the zeolite lattice ( $\text{O}^{2-}$ ), and basic OH groups.<sup>38,60–62</sup> HNaY zeolite has approximately the same strong proton centers as HZSM, but their content is higher (about 800  $\mu\text{mol/g}$ ). The content of strong Lewis acid centers is also higher. The concentration of basic centers is higher as well and amounts to about 1500  $\mu\text{mol/g}$ .<sup>63</sup> IR spectroscopic data show that the initial Na zeolites contain practically no proton centers, have weak Lewis acid centers,  $\text{Na}^+$  cations, and basic centers ( $\text{O}^{2-}$ ), whose amount is 100–300  $\mu\text{mol/g}$ .<sup>63</sup>

Highly siliceous zeolites HZSM are active in the methanol reaction with  $\text{H}_2\text{S}$  and highly selective towards dimethyl sulfide, but possess low selectivity towards methanethiol. The formation mechanisms of the sulfide have been suggested to be different (Scheme 2). A certain probability of route 6 cannot be ruled out, but since the content of Lewis acid centers in HZSM is slightly lower than that of proton centers, the surface coverage by SH fragments is small and cannot sustain the high formation rates of the sulfide as observed in the experiments. It is more probable that a major part of the dimethyl sulfide formed on HZSM is obtained from the reaction of  $\text{CH}_3\text{O}$  groups with  $\text{H}_2\text{S}$ , either gaseous or associatively adsorbed on HZSM (route 3, Scheme 2).

As the ratio Si/Al in HZSM increases, the reaction rate and the selectivity towards the sulfide drop, whereas the selectivity towards dimethyl ether rises, since the concentration of strong proton-donor centers responsible for the surface methoxylation decreases.<sup>62</sup> On other catalysts with weaker proton-donor and basic centers the formation rate of sulfur-containing compounds is low and the selectivity towards dimethyl ether is increased. For example,<sup>15,17</sup> in the presence of  $\text{SiO}_2$  with weak surface proton-donor centers (cf. Table 2), the main reaction product at 360 °C is dimethyl ether with only traces of methanethiol and dimethyl sulfide, even with long contact times. The addition to  $\text{SiO}_2$  of phosphoric or sulfuric acid leads to the appearance of stronger surface proton-donor centers compared to  $\text{SiO}_2$ . In this case no other centers are found (Table 2). The reaction rate rises compared to  $\text{SiO}_2$ , but the yield of dimethyl sulfide is very low and the main product is dimethyl ether. The yield of the sulfide cannot be increased by temperature variations. With increasing contact time from 8 to 42 s in the presence of a  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst, the methanol conversion increases, the selectivity towards the ether drops from 100 to 75%, that towards the sulfide rises, but even at  $X = 100\%$  the selectivity is less than 25%. The total activity of these catalysts compared to HZSM is an order of magnitude or even more lower. Apparently, this is due to the fact that these catalysts have weaker acid and basic centers. The total ratio of methanol per proton center ( $W_{\text{H}^+}$ ) decreases in the sequence:

$$\begin{array}{cccc} \text{HZSM} & > & \text{H}_3\text{PO}/\text{SiO}_2 & > & \text{SiO}_2 \\ W_{\text{H}^+} & & 0.4\text{--}0.7 & & 0.1 & & 0.002 \end{array}$$

The same sequence is observed for the decrease in the strength of proton-donor centers and catalyst basicity (Table 2).

In the presence of HZSM the rate of methanethiol formation is low and the selectivity towards the thiol changes only slightly with varying Si/Al. The kinetic data imply that the formation of methanethiol on HZSM follows a different route than that of dimethylsulfide. Without ruling out a possible participation of molecular  $\text{H}_2\text{S}$  in the thiol

synthesis according to Scheme 2 (route 2)<sup>18,19</sup> it can be assumed that a more energetically advantageous route is route 5 of Scheme 2 with the participation of SH fragments bound to strong Lewis acid centers. Since the content of these centers in HZSM is low, the surface coverage by SH<sup>-</sup> structures is not high and this accounts for the low rate of methanethiol formation.

The HNaY zeolite contains a larger number of strong Lewis acid centers than HZSM. This promotes an increase of the surface coverage by SH fragments and hence a certain increase in the selectivity towards methanethiol as compared to HZSM. The high concentrations of strong Lewis centers in HNaY may also be responsible for the increased catalyst selectivity towards dimethyl ether as compared to HZSM. A partial consumption of methanol for the formation of methanethiol and dimethyl ether accounts for the decreased (by a factor of 2–3) selectivity towards dimethyl sulfide on HNaY as compared to HZSM. A reason for the decrease (by a factor of 2–4) in the total reaction rate of methanol on HNaY is unclear. Apparently, it can be ascribed to the deactivation of this catalyst by coke formation.

The sodium forms of zeolites are less active compared to decationated ones. For example, the total activity of NaY is lower by a factor of 10–20 (depending on the reactant concentrations) than that of HNaY and that of NaX is half that of HNaY. The selectivity towards the sulfide on sodium zeolites is the same as on HNaY, but they are considerably (5–8 times) more selective towards methanethiol formation (Table 5).

The original Na zeolites possess practically no proton centers, but such centers can be formed under the effect of the reaction medium (cf. p. 285). The NaX zeolite is readily protonated by H<sub>2</sub>S, whereas on NaY this process is hindered at adsorption temperatures up to 100 °C, but can be induced at higher temperatures. The proton centers generated can take part in methanol activation to produce CH<sub>3</sub>O groups. These groups react with molecular H<sub>2</sub>S to form the sulfide, i.e. the reaction follows the same mechanism as that on decationated zeolite. Therefore the selectivity towards the sulfide on Na zeolites and e.g. HNaY is approximately the same. As mentioned above, the yield of methanethiol from this process is low even with excess H<sub>2</sub>S in the system. It is more probable that methanethiol is produced by the reaction of CH<sub>3</sub>O groups with SH fragments (Scheme 2, route 5) bound to sodium cations. The concentration of SH fragments on Na zeolites is higher than on HNaY containing largely proton centers, which accounts for the increased selectivity towards methanethiol on Na zeolites. The total concentration of surface active sites on Na zeolites is lower than on HNaY, hence they have a decreased total activity in the reaction of methanol with H<sub>2</sub>S.

The total activity of NaX zeolites is 7–9 times higher than that of NaY, but the selectivity of these catalysts towards the thiol and the sulfide is approximately the same. It can be suggested that during interaction of methanol with H<sub>2</sub>S an important role is played by delocalized sodium cations, which are more numerous on NaX than on NaY.<sup>49</sup> Besides, NaX possesses a higher basicity than NaY.<sup>63</sup> As a result, the total activity of the former is considerably higher than that of the latter. The similar selectivity towards the formation of methanethiol and dimethyl sulfide on NaX and NaY indicates the same mechanism of the reaction of methanol with H<sub>2</sub>S on these catalysts.

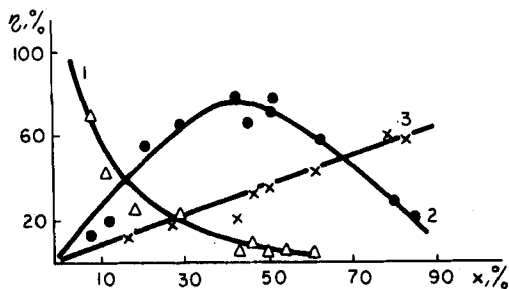
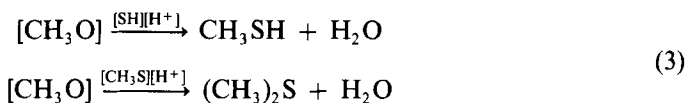
SiO<sub>2</sub> samples with acid Cr<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, and WO<sub>3</sub> additives contain, besides strong proton centers (C = 30–100 μmol/g), weak Lewis acid centers (Q<sub>CO</sub> ~ 28 kJ/mol, C ~ 200 μmol/g), and basic centers of moderate strength (PA ~ 800 kJ/mol). The



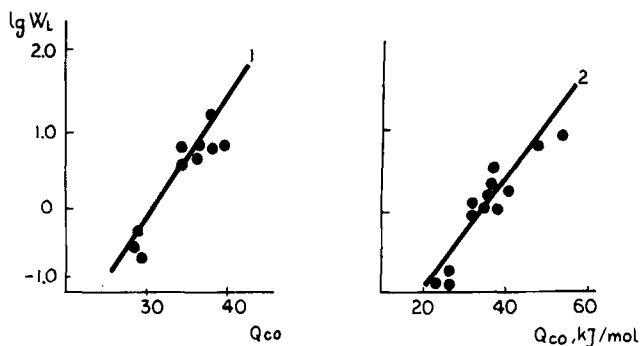
**Table 6.** Catalyst activity and selectivity in the reaction of methanol with H<sub>2</sub>S  
 T = 360 °C, H<sub>2</sub>S:CH<sub>3</sub>OH = 0.6–1.6, X<sub>methanol</sub> = 70–80%<sup>15–17</sup>

| Catalysts  | H <sub>2</sub> S:CH <sub>3</sub> OH = 0.6 |                    |   | H <sub>2</sub> S:CH <sub>3</sub> OH = 1.6 |                    |   |
|--|---|--------------------|---|---|--------------------|---|
|  | Activity, v<br>mmol<br>g·h                | CH <sub>3</sub> SH | Selectivity<br>(%)<br>(CH <sub>3</sub> ) <sub>2</sub> S | Activity, v<br>mmol<br>g·h                | CH <sub>3</sub> SH | Selectivity<br>(%)<br>(CH <sub>3</sub> ) <sub>2</sub> S |
| SiO <sub>2</sub>   | 5   | 2                  | 6   | 2   | 25                 | 6   |
| SiO <sub>2</sub> + 6–30% H <sub>3</sub> PO <sub>4</sub> ;<br>5% H <sub>2</sub> SO <sub>4</sub>   | 5–34                                      | 1–5                | 3–10  | 4–6                                       | 1–3                | 20–30   |
| AlSi, HNaY   | 6–7                                       | 1–5                | 70–90   | 15–20                                     | 6–7                | 20–60   |
| HZSM   | 214                                       | 4                  | 96  | 250                                       | 20                 | 80  |
| NaX  | 8   | 44                 | 56  | 4   | 17                 | 83  |
| SiO <sub>2</sub> + 1.0–2.5% Cr <sub>2</sub> O <sub>3</sub> ;<br>4–15% MoO <sub>3</sub> ; 7–10%<br>WO <sub>3</sub>  | 5–40                                      | 20–40              | 50–70   | 15–30                                     | 30–70              | 20–60   |
| γ-, η-Al <sub>2</sub> O <sub>3</sub> and<br>Al <sub>2</sub> O <sub>3</sub> + 1–5% Cr <sub>2</sub> O <sub>3</sub> ;<br>4–20% MoO <sub>3</sub> ; 10% V <sub>2</sub> O <sub>5</sub> ;<br>4–24% WO <sub>3</sub>                  | 200–1000                                  | 10–20              | 70–80   | 600–1100                                  | 25–50              | 30–60   |
| Al <sub>2</sub> O <sub>3</sub> + 4–20% K <sub>2</sub> CO <sub>3</sub> ;<br>4.5% Na <sub>2</sub> CO <sub>3</sub> ; 5% KOH;<br>1–4% NaOH; 10–25%<br>K <sub>2</sub> WO <sub>4</sub> ;<br>10–15% Na <sub>2</sub> WO <sub>4</sub> | 2–4                                       | 65–83              | 17–35   | 4–17                                      | 70–98              | 1–18  |
| SiO <sub>2</sub> + 4–20% K <sub>2</sub> CO <sub>3</sub> ;<br>25% K <sub>2</sub> WO <sub>4</sub>  | 2–4                                       | 70–96              | 8–35  | 3–8                                       | 82–98              | 8–15  |

activity of these catalysts is higher than that of the NaX zeolite (Table 6). The dependence of the selectivities towards the different products indicates that the consecutive reactions follow Scheme 3 with the participation of CH<sub>3</sub>O, SH, and CH<sub>3</sub>S fragments (Figure 1):



**Figure 1.** The influence of the degree of methanol conversion on Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> selectivity towards dimethyl ether (1), methanethiol (2), and dimethyl sulfide (3) at 360 °C.<sup>17</sup>

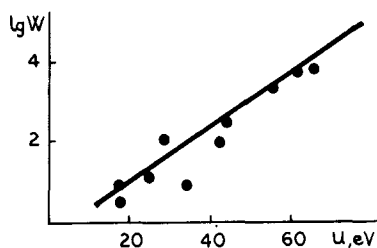


**Figure 2.** The logarithmic dependence of the catalyst activity ( $v \cdot 10 \text{ mmol/g} \cdot \text{h}$ ) per one Lewis acid center on this center strength,  $T = 360^\circ\text{C}$ ,  $\text{H}_2\text{S}:\text{CH}_3\text{OH} = 0.6$  (1) and 1.6 (2).<sup>15,17</sup>

An increase in the reaction rate is also observed on catalysts with paired acid-basic centers:  $\gamma$ - and  $\eta$ - $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{MoO}_3/\text{Al}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ , and  $\text{WO}_3/\text{Al}_2\text{O}_3$ . Their surfaces contain considerable concentrations ( $C = 400\text{--}800 \mu\text{mol/g}$ ) of strong Lewis acid centers ( $Q_{\text{CO}} = 33\text{--}42 \text{ kJ/mol}$ ) and moderately basic centers ( $C = 100\text{--}800 \mu\text{mol/g}$ ,  $\text{PA}^b = 800\text{--}900 \text{ kJ/mol}$ ). They also contain strong proton-donor centers with  $\text{PA}^d < 1300 \text{ kJ/mol}$ ,  $C \sim 50 \mu\text{mol/g}$ , except  $\text{Al}_2\text{O}_3$  where no such centers can be found according to its pyridine adsorption. An increase in the strength of the Lewis acid centers and in their surface concentration increases the total activity of catalysts (Table 6). The total reaction rate of methanol per Lewis center rises with increasing Lewis acid strength of these sites (Figure 2). The quantitative correlation is less than satisfactory, apparently due to the fact that the participation in the reaction of centers having different strengths and a certain contribution to processes at some other active centers, e.g. proton-donor and basic ones, are not taken into account.

Experiments with compact oxides confirm the participation of acceptor centers in the acceleration of the reaction. As can be seen from Figure 3, the total reaction rate of methanol per  $\text{m}^2$  surface of the samples grows with increasing ionization potential of the cations, i.e. it depends on the cation acceptability.

The role of moderately basic centers contained in the catalysts along with acid ones has been established by comparison of  $\text{Al}_2\text{O}_3$  and  $\text{HF}/\text{Al}_2\text{O}_3$  samples.<sup>15,17</sup> In the fluorine promoted sample the concentration and strength of the basic centers are decreased; it has a certain amount of strong proton-donor centers; besides acid centers, e.g. those like



**Figure 3.** The activity of bulk samples per unit surface ( $v \cdot 10^2 \text{ mmol/m}^2 \cdot \text{h}$ ) vs. ionization potentials.<sup>15</sup>

in  $\text{Al}_2\text{O}_3$ , there appear stronger Lewis acid centers (Table 2). The total reaction rate on  $\text{HF}/\text{Al}_2\text{O}_3$  is one third of that on  $\text{Al}_2\text{O}_3$ . The selectivity towards dimethyl sulfide also diminishes, whereas that towards dimethyl ether rises. For example, at a methanol conversion of 75%, the selectivity towards the sulfide equals 14 and 55% on  $\text{HF}/\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , respectively. Only when the methanol conversion reaches 95%, which is achieved with a contact time three times higher than that on  $\text{Al}_2\text{O}_3$ , the selectivity on  $\text{HF}/\text{Al}_2\text{O}_3$  becomes the same as on  $\text{Al}_2\text{O}_3$  (90%). These data indicate the importance of the presence of strong centers in the conjugated acid-base pair promoting the dissociative chemisorption of the reactants to form  $\text{SH}^-$ ,  $\text{OH}^-$ , and  $\text{CH}_3\text{O}^-$  species.

The introduction into the catalyst of additives decreasing its acidity and increasing considerably its surface basicity is unfavorable for the catalyst activity in the formation of dimethyl sulfide from methanol and  $\text{H}_2\text{S}$ .<sup>13-17</sup> Upon the introduction into  $\text{Al}_2\text{O}_3$  of potassium or sodium hydroxide, carbonate, and tungstate, the proton centers are suppressed, the concentration of Lewis acid centers decreases ( $C = 100\text{--}400 \mu\text{mol/g}$ ), and their strength diminishes ( $Q_{\text{CO}} = 28\text{--}31 \text{ kJ/mol}$ ). Besides basic centers like in  $\text{Al}_2\text{O}_3$  with  $\text{PA}^b \sim 800\text{--}900 \text{ kJ/mol}$ , there appear stronger ones with  $\text{PA}^b \sim 920\text{--}900 \text{ kJ/mol}$  ( $C = 100\text{--}70 \mu\text{mol/g}$ ) and with  $\text{PA}^b = 925\text{--}970 \text{ kJ/mol}$  ( $C = 200\text{--}500 \mu\text{mol/g}$ ).<sup>16</sup> Studies of  $\text{Al}_2\text{O}_3$  samples modified by bases (2 wt. % of alkali or alkaline earth metal oxides) revealed a rate decrease in the reaction of methanol with  $\text{H}_2\text{S}$ . The greatest effect is produced by alkali metal oxides,<sup>9</sup> which has also been confirmed by some other authors.<sup>16,17</sup>

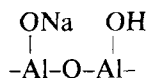
The sharpest decrease in  $\text{Al}_2\text{O}_3$  activity is observed<sup>64</sup> upon introduction of very small amounts of additive, e.g. about 0.1 wt. %  $\text{NaOH}$  (Table 7).  $\gamma\text{-Al}_2\text{O}_3$  has no strong proton-donor centers since pyridine adsorption gives no pyridinium ions according to the IR spectrum. If one uses ammonia as test compound, i.e. a stronger base than pyridine, the IR spectrum exhibits bands typical for asymmetric deformational vibrations of  $\text{NH}_4^+$  ( $\sim 1460 \text{ cm}^{-1}$ ) formed by interaction of ammonia with proton centers (OH groups with a band at about  $3770 \text{ cm}^{-1}$ ). Acid OH groups are also found according

**Table 7.** The effect of alkali metal additives on  $\text{Al}_2\text{O}_3$  activity in the reaction of methanol with  $\text{H}_2\text{S}$ ;  $T = 360^\circ\text{C}$ , methanol conversion 60%

| Concentration of additive to $\text{Al}_2\text{O}_3$ (wt.%) (mg-at/g) |      | $\text{H}_2\text{S}:\text{CH}_3\text{OH} = 0.6$ |                                | $\text{H}_2\text{S}:\text{CH}_3\text{OH} = 1.6$ |                                |
|---|------|---|--------------------------------|---|--------------------------------|
|   |      | Contact time (s)                                | Relative activity* $v/v_0$ (%) | Contact time (s)                                | Relative activity* $v/v_0$ (%) |
| 0   | 0    | 0.064   | 100                            | 0.06  | 100                            |
| 0.1   | 25   | 0.1   | 25                             | 0.1   | 30                             |
| 0.4   | 100  | 1.0   | 6.5                            | 0.7   | 8.6                            |
| 1.0   | 250  | 2.5   | 2.6                            | 1.9   | 3.1                            |
| 3.0   | 750  | 20  | 0.3                            | 10  | 0.6                            |
| 12.0  | 3000 | 50  | 0.1                            | 15  | 0.4                            |
| $\text{K}_2\text{WO}_4/\text{Al}_2\text{O}_3$                         |      |   |                                |   |                                |
| 2.5   | 153  | 1.7   | 3.7                            | 1.2   | 5.0                            |
| 5.0   | 307  | 4.2   | 1.5                            | 3.2   | 2.0                            |
| 10.0  | 614  | 20  | 0.3                            | 7.0   | 0.9                            |

\*  $v$  and  $v_0$  are the activities of a given sample and of unpromoted  $\text{Al}_2\text{O}_3$ , respectively.

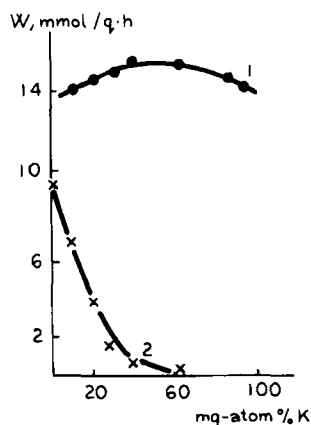
to the CO adsorption, but in smaller concentrations ( $C = 0.2\text{--}0.3 \mu\text{mol}/\text{m}^2$ ). The addition of alkali metal (K, Na, Li) hydroxides decreases the concentration of proton centers. In this case a hydrogen ion of a surface hydroxyl group is substituted by an alkali metal ion. Apparently, the surface of  $\text{Al}_2\text{O}_3$  is simultaneously hydroxylated by OH groups of the alkali. As a result there form surface structures



With small amounts of alkaline additives (less than  $75 \mu\text{mol}/\text{g}$ ) only proton centers are affected. Larger amounts of additives also affect Lewis acid centers.<sup>64</sup> It is possible that small additions of alkali suppress very strong Lewis acid centers which are present in  $\text{Al}_2\text{O}_3$  in low concentration. The presence of acid centers in  $\text{Al}_2\text{O}_3$  is important for surface methoxylation, since upon their suppression the concentration of  $\text{CH}_3\text{O}$  groups decreases, which diminishes the reaction rate.

Depending on the nature of the additive and its concentration, the total activity and that towards methanethiol (at a conversion of 70–80%) decreases compared to  $\text{Al}_2\text{O}_3$  1–1.5 orders of magnitude and by 2–4 orders of magnitude towards dimethyl sulfide. The selectivity towards the sulfide decreases to 15–35% compared to  $\text{Al}_2\text{O}_3$  (70–80%). Thus, catalysts direct the reaction towards the formation of methanethiol (Table 6).

As the content of potassium carbonate or tungstate on  $\text{Al}_2\text{O}_3$  rises, the surface acidity and the activity in dimethyl sulfide formation diminish.<sup>14,16</sup> The selectivity of tungstate samples towards the sulfide slightly increases if instead of sodium tungstate  $\text{Na}_2\text{WO}_4$ , polytungstates, hexa-, dodeca- or metatungstate  $\text{Na}_6\text{W}_7\text{O}_{24}$ ,  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$ , and  $\text{Na}_6\text{H}_4[\text{H}_2\text{W}_{12}\text{O}_{42}]$ , respectively (with the concentrations:  $[\text{W}] = 30.7$ ,  $[\text{Na}] = 23.3$ , 25.7 and 15.4 mg-at.%) are used. Addition of sodium carbonate to the polytungstate sample corresponding to a sodium content  $[\text{Na}] = 61.4 \text{ mg-at.}\%$  produces a catalyst whose activity and selectivity towards the formation of dimethyl sulfide is close to that obtained by the application of sodium tungstate. The differences in the activity and selectivity of polytungstate samples is thus due to the different concentrations of sodium.



**Figure 4.** The effect of  $\text{WO}_3/\text{Al}_2\text{O}_3$  modification with  $\text{K}_2\text{CO}_3$  on the formation rate of methanethiol (1) and dimethyl sulfide (2) ( $360^\circ\text{C}$ ,  $\tau = 4.2 \text{ s}$ ).<sup>16</sup>

Upon addition of potassium carbonate to the acid catalyst 7%  $\text{WO}_3/\text{Al}_2\text{O}_3$  with strongly acid and moderately basic centers its selectivity towards the sulfide decreases (Figure 4).

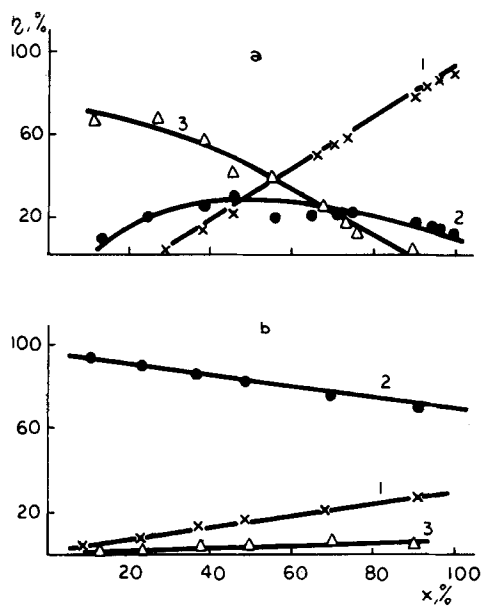
The type of the alkaline additive exerts a certain effect on the acid-base and catalytic properties of the samples.<sup>16</sup> Catalysts modified by potassium or sodium at the same atomic concentrations differ slightly in the concentration and strength of Lewis acid centers. A certain effect is caused by the nature of the anion: the concentration of Lewis acid centers decreases in the sequence: carbonate > hydroxide > tungstate. The same order is observed for a slight increase in the strength of the acid centers. With increasing concentration of alkaline additives the strength of the acid centers slightly decreases, whereas their concentration remains almost unchanged.

Moderately basic centers are present in similar concentrations in all samples examined, but their strength in  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  and  $\text{KOH}/\text{Al}_2\text{O}_3$  ( $\text{PA}^b = 850\text{--}860$  kJ/mol) and in  $\text{NaOH}/\text{Al}_2\text{O}_3$  ( $\text{PA}^b = 830$  kJ/mol) is higher than in the rest of the samples ( $\text{PA}^b = 800$  kJ/mol). The concentration of the basic centers with  $\text{PA}^b = 800\text{--}850$  kJ/mol diminishes with decreasing concentration of the alkali metal in the catalysts. The surfaces of all samples possess basic centers with  $\text{PA}^b = 925\text{--}930$  kJ/mol and their concentration at the same atomic content of alkali metals in  $\text{NaOH}/\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{WO}_4/\text{Al}_2\text{O}_3$  is 1.5–2 times higher than in the remaining samples. Tungstate samples contain basic centers with  $\text{PA} = 900\text{--}910$  kJ/mol absent in the other catalysts.  $\text{Al}_2\text{O}_3$  modified with sodium or potassium carbonate or hydroxide contains strongly basic centers ( $\text{PA}^b = 950\text{--}970$  kJ/mol) not detected on tungstate samples.

Thus, the strongest basic properties are observed for  $\text{Al}_2\text{O}_3$  promoted by potassium or sodium carbonate or hydroxide and the samples containing potassium are slightly more basic than sodium-containing catalysts. Tungstate samples contain less basic centers. The total concentration of basic centers with  $\text{PA} = 900\text{--}970$  kJ/mol is, however, approximately the same for all catalysts examined possessing an equal atomic content of alkali metals.

Slight changes are also observed<sup>16,17</sup> in the catalytic properties with variation of the type of alkaline modifiers. The total activity of sodium- or potassium-containing samples is practically the same. No noticeable effect of the nature of the anion is observed either, but the selectivities towards dimethyl sulfide differ slightly. The samples containing sodium are slightly more selective towards the sulfide than the potassium catalysts. Hydroxide- and carbonate-containing samples which are of higher basicity possess a higher selectivity than tungstate catalysts. Besides strongly basic centers these catalysts possess weak Lewis acid centers. The activity of the Lewis acid centers drops more sharply than could be expected from the  $\lg W_L$  vs.  $Q_{\text{CO}}$  curve (Figure 2).

In order to establish the feasibility of the methanol reaction with  $\text{H}_2\text{S}$  under the effect of strongly basic centers,  $\text{SiO}_2$  samples modified by alkali metal compounds have been examined.<sup>16</sup> The surface of these catalysts contains basic centers with  $\text{PA}^b = 800\text{--}900$  and  $960\text{--}970$  kJ/mol ( $C = 300\text{--}400$   $\mu\text{mol/g}$ ) and also weak Lewis acid centers, sodium or potassium cations. Compared to  $\text{SiO}_2$ , the activity of catalysts containing e.g. 4–20 wt. %  $\text{K}_2\text{CO}_3$  or  $\text{K}_2\text{WO}_4$  on  $\text{SiO}_2$  increases: the total activity 1.4–4 times, that towards the sulfide 2–10 times and that towards the thiol 5–10 times and an increased selectivity towards sulfur-containing products compared to the original support is observed (Table 6). This effect is stronger the higher the concentration of the alkali metal



**Figure 5.** The influence of methanol conversion on the selectivity towards dimethyl sulfide (1), methanethiol (2), and dimethyl ether (3) at  $\text{H}_2\text{S}:\text{CH}_3\text{OH} = 0.6$ . (a)  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $T = 320^\circ\text{C}$ , (b)  $\text{K}_2\text{WO}_4/\text{Al}_2\text{O}_3$ ,  $T = 360^\circ\text{C}$ .<sup>16</sup>

compound on  $\text{SiO}_2$ . Under various experimental conditions the main product on these catalysts is the thiol; the selectivity towards dimethyl sulfide is as high as 35%, i.e. the same as in the presence of  $\text{Al}_2\text{O}_3$  modified by alkali metal compounds.

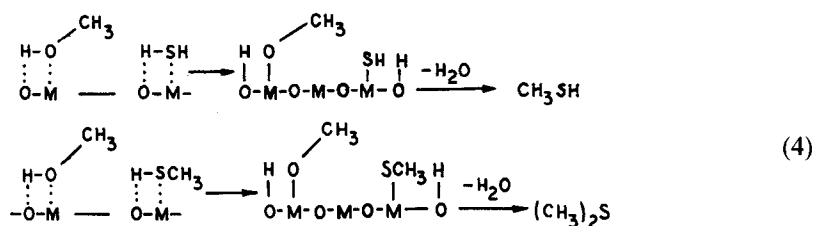
The reaction of methanol with  $\text{H}_2\text{S}$  also takes place on compact  $\text{Na}_2\text{WO}_4$  and  $\text{K}_2\text{CO}_3$  samples without acid centers and the main reaction product is methanethiol.<sup>16</sup> The total activity of these catalysts per unit surface ( $W = 0.2\text{--}0.3 \mu\text{mol}/\text{m}^2$ ) is higher than that of samples containing 3 wt. %  $\text{NaOH}$  or 10–15 wt. % potassium or sodium tungstate on  $\text{Al}_2\text{O}_3$  ( $W = 0.04 \mu\text{mol}/\text{m}^2$ ), though the latter samples contain, besides basic, acid centers as well.

As seen from the curves of the selectivity towards products vs. methanol conversion (Figure 5), the primary sulfur-containing product on alkaline catalysts is methanethiol and its further reaction leads to dimethyl sulfide formation. The methanol activation can involve the participation of strong basic, weak Lewis acid or proton centers generated on the surface of the  $\text{Al}_2\text{O}_3$  catalyst due to  $\text{H}_2\text{S}$  decomposition on acid-basic pairs of centers (“strongly basic—weakly acid centers”). It can be suggested that in the presence of basic catalysts as well as of acid catalysts methanethiol formation follows Scheme 2, route 5, i.e. it occurs via the interaction of SH fragments with the methoxyl groups formed from methanol or ether. Further methanol conversion requires their dissociative chemisorption to form  $\text{CH}_3\text{S}$  fragments whose reaction with  $\text{CH}_3\text{O}$  groups will produce dimethyl sulfide (Scheme 2, route 7). At a relatively low concentration of basic centers the surface can preserve a certain amount of acid centers taking part in thiol activation. In the absence of acid centers the thiol is activated by basic ones. On the latter the

process is hindered due to the lower acidity of the thiol compared to  $H_2S$ . Therefore, on catalysts with strongly basic centers the main product is methanethiol rather than dimethyl sulfide. It is still probable that the sulfide is formed according to Scheme 2, routes 3 and 4, in the reaction of  $CH_3O$  groups with weakly activated  $H_2S$  or thiol. But as mentioned above, this process is energetically less favorable than that with the participation of more reactive SH fragments. Thus, the low formation rate of dimethyl sulfide on catalysts having strongly basic and weak Lewis acid centers is due to the slow activation of methanethiol and the predominant reaction of  $CH_3O$  groups with SH fragments which are present on the surface in considerable concentration. Sulfide formation is more favorable in the presence of surface pairs of "strongly acid—moderately basic centers".

Additional data on the formation mechanism of dimethyl sulfide from methanol and  $H_2S$  on  $Al_2O_3$  catalysts were obtained from kinetic studies. Under the effect of acid  $Al_2O_3$  catalysts increasing contact time leads to an increase in methanol conversion and dimethyl sulfide yield, the yield of dimethyl ether drops and that of methanethiol rises to a certain value and then falls. The analysis of the selectivity vs. methanol conversion curves shows that the primary sulfur-containing reaction product is methanethiol and the secondary one is dimethyl sulfide (Figure 5).

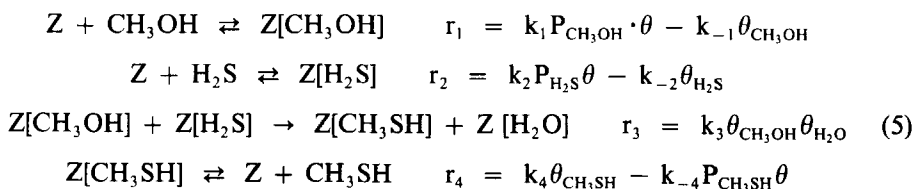
The process can be described by the scheme:

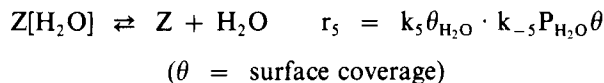


Interaction of the methoxyl groups with SH fragments produces methanethiol. The latter is a stronger base than  $H_2S$  and is predominantly adsorbed on the catalyst to form  $\text{OH}^-$  and  $\text{CH}_3\text{S}^-$  fragments whose reaction with  $\text{CH}_3\text{O}^-$  produces dimethyl sulfide. As a result of the above sequence of reactions on  $Al_2O_3$  catalysts it is impossible to obtain methanethiol with high selectivity, whereas the dimethyl sulfide forms with almost 100% selectivity. A similar reaction is also observed on  $Al_2O_3$  catalysts modified by alkali, but step 2 of Scheme 4 is hindered.

When a kinetic equation to describe the formation of methanethiol and dimethyl sulfide on  $Al_2O_3$  catalysts is required it is suggested to follow Scheme 4.

Methanethiol is obtained as a result of the following elementary steps:





Here Z is an active center,  $[CH_3OH]$  and  $[H_2S]$  are dissociatively chemisorbed methanethiol and  $H_2S$  with the formation of  $CH_3O$ ,  $OH$  and  $SH$  fragments. The first two steps are the sum of several fast steps including the dissociation of the initial reactants. Assuming that the limiting step is the interaction of surface groups to form methanethiol and water, the following equation for the reaction rate of methanol conversion to methanethiol is obtained:

$$W = \frac{K P_{CH_3OH} P_{H_2S}}{(1 + b_1 P_{CH_3OH} + b_2 P_{H_2S} + b_3 P_{CH_3SH} + b_4 P_{H_2O})^2}$$

where  $b_1 = k_1/k_{-1}$ ;  $b_2 = k_2/k_{-2}$ ;  $b_3 = k_{-4}/k_4$ ;  $b_4 = k_{-5}/k_5$ ;  $K = k_3(k_1/k_{-1}) \cdot (k_2/k_{-2})$ .

Dimethyl sulfide formation from methanol and methanethiol takes place through a similar sequence of elementary steps. The kinetic equation is the same as that for the methanethiol formation, but with other numerical constants.

The reaction of methanol with  $H_2S$  in the presence of  $Al_2O_3$  modified by alkaline additives is described by similar equations.

The suggestion of participation of surface methoxy groups and activated  $H_2S$  in the formation of methanethiol and dimethyl sulfide is supported by IR and NMR studies.<sup>18,19,34,36</sup>

Upon admitting  $H_2S$  to HNaY sample with adsorbed methanol on its surface one can observe changes in the IR spectrum: the intensities of the bands typical for adsorbed  $H_2S$  ( $SH^-$ ,  $2560-2580\text{ cm}^{-1}$  and acid  $OH$ ,  $3550-3650\text{ cm}^{-1}$ ) and for  $CH_3O$  groups ( $2850$ ,  $2940$ , and  $1460\text{ cm}^{-1}$ ) decrease. At the same time there appear bands typical for adsorbed methanethiol and dimethyl sulfide ( $2880$ ,  $3020$ ,  $1425$ , and  $1275\text{ cm}^{-1}$ ). Similar results were obtained in studies of methanol interaction with  $H_2S$  catalyzed by HZSM,  $Al_2O_3$ ,  $Cr_2O_3/Al_2O_3$ ,  $NaOH/Al_2O_3$  and  $K_2CO_3/SiO_2$ .

In accordance with the NMR data, on  $SiO_2$ ,  $H_3PO_4/Si_2O$  and NaY catalysts at various degrees of surface coverage and on HZSM, NaX, and  $Al_2O_3$  at monolayer coverage methanol is adsorbed without decomposition: the  $^{13}C$  and  $^1H$  NMR spectra exhibit signals at  $\delta = 54$  and  $\delta = 2.0, 4.5$  ppm ( $CH_3$  and  $OH$  groups, respectively). At low surface coverages on HZSM, NaX and  $Al_2O_3$  one can also observe dissociative adsorption of methanol to form methoxyl groups (a signal with  $\delta = 60$  ppm in the  $^{13}C$  NMR spectrum). On  $Al_2O_3$  this adsorption is predominant. Upon admitting  $H_2S$  to the sample with preadsorbed methanol one can observe first broadening of the signal from the adsorbed undecomposed methanol without noticeable changes in chemical shifts or appearance of new signals (e.g., on NaY). After temperature elevation one can observe a decrease in the intensity of the signal belonging to  $CH_3O$  groups and of those typical for molecular  $H_2S$  and  $SH$  groups (lines with  $\delta = 1.0$  and  $1.6-3.6$  ppm, respectively, in the  $^1H$  NMR spectrum). Simultaneously there appear signals of the products formed: dimethyl ether (a signal with  $\delta = 3.0$  ppm in the  $^1H$  NMR spectrum) and methanethiol and dimethyl sulfide (signals with  $\delta = 6$  and  $18$  ppm, respectively, in the  $^{13}C$  NMR spectrum).

Much less comprehensively studied is the reaction of  $H_2S$  with methanol homologs.



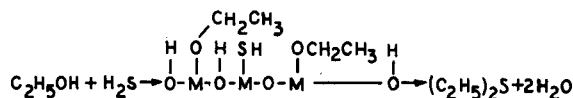
In the presence of  $\text{Al}_2\text{O}_3$  at atmospheric pressure and contact times of 5–6 s the interaction of  $\text{H}_2\text{S}$  with ethanol and *n*-octanol with excess concentration relative to alcohol (2.9–7.7, respectively) at 317 °C, takes place mainly with the formation of ethanethiol. The selectivity towards the thiol is 46–34%, the yield of sulfide is as high as 2 mol. %, the reaction produces ethers and olefins. The total rate of octanol conversion is higher than that of ethanol.<sup>9</sup> Under the same conditions on  $\text{Al}_2\text{O}_3$  modified with potassium tungstate the rate of octanol formation is also higher than that of ethanol. The selectivity towards the thiol increases compared to that observed on  $\text{Al}_2\text{O}_3$ , up to 68–77%. The yield of the sulfide rises up to 5 mol. % and those of olefin and ether are lower than on  $\text{Al}_2\text{O}_3$ . With temperature elevation the alcohol conversion increases and the yield of the sulfide drops whereas that of olefin rises. Under similar conditions the yield of olefin from octanol is higher than from ethanol.<sup>9</sup> Similar results are also obtained on  $\text{Al}_2\text{O}_3$  catalysts modified with K, Na, and W oxides (sulfurized with  $\text{H}_2\text{S}$  at 350 °C for 12 h) in the interaction of *n*-propanol with  $\text{H}_2\text{S}$  at 300 °C and contact times of 0.1–1 s. Under these conditions the main products are 1-propanethiol, dipropyl ether and propylene. The selectivity towards dipropyl sulfide is as high as 5 mol. %.<sup>65</sup> Ethanol conversion has been studied<sup>66</sup> in a methane and  $\text{H}_2\text{S}$  medium catalyzed by NaX, NaY, CaX, HY and REY zeolites at 350 °C and  $P = 0.6\text{--}3.0$  MPa. With large excess of  $\text{H}_2\text{S}$  relative to alcohol the main product is ethanethiol, no sulfide formation was observed. In the presence of NaX, NaY, HNaY, NaZSM-5, and HZSM-5 zeolites at 250 and 350 °C, a ratio  $\text{H}_2\text{S}:\text{alcohol} = (1\text{--}4):1$  and contact times of 1–3 s the main product of the  $\text{H}_2\text{S}$  reaction with ethanol and propanol was the thiol and the yield of the sulfide was considerably lower. The selectivity towards the combined yield of thiol and sulfide from ethanol is higher than that from propanol.<sup>67</sup> The reaction with ethanol also produces ethanethiol and diethyl sulfide, that with propanol also produces, besides 1-propanethiol and dipropyl sulfide, ethanethiol, 2-propanethiol and dimethyl sulfide. According to their activity the zeolites examined are arranged in the sequence:



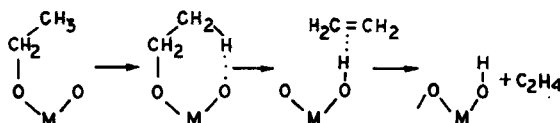
This means that NaX is considerably more active than the rest of the zeolites. It is suggested that alcohol thiolation is promoted by the presence of surface SH and acid OH groups formed by the dissociative chemisorption of  $\text{H}_2\text{S}$ , and the presence of sodium cations in the zeolite. The low activity of the remaining catalysts towards sulfide and thiol is due to alcohol decomposition. It has been concluded<sup>67</sup> that sodium cations are active centers with respect to thiol formation while proton centers make an essential contribution to sulfide formation.

Thus, with increasing molecular weight of the alcohol the total reaction rate of the alcohol rises, but the selectivity towards the sulfide drops due to alcohol dehydration.

A first step in the alcohol reaction with  $\text{H}_2\text{S}$  is the formation of surface alkoxide groups reacting with  $\text{H}_2\text{S}$  to form thiol and sulfide according to Scheme 6, similar to that for methanol. In the case of higher alcohols, still another reaction route, i.e. decomposition of the alkoxy group is possible:<sup>22</sup>



(6)



The olefin formed by the alcohol dehydration can react with  $H_2S$  to produce the thiol and the sulfide.

The addition of  $H_2S$  to alkenes to form sulfides has been comprehensively studied in solution under the effect of strong mineral acids: hydrochloric, sulfuric, phosphoric, hydrofluoric and alkanesulfonic acids; Friedel-Crafts catalysts:  $AlCl_3$ ,  $BF_3$ ,  $TiCl_4$ ,  $SbCl_5$ ,  $ZnCl_2$ , and  $SnCl_4$ ; bases: amines, potassium and sodium hydroxide. Apart from the major reaction, secondary reactions such as isomerization, cracking, and polymerization of the initial olefin also take place.<sup>68,69</sup>

This heterogeneous process takes place at 150–400 °C. It is promoted by phosphoric, sulfuric, molybdeno-, phosphoro- or silicotungstic and borotungstic acid supported on  $SiO_2$ ,  $Al_2O_3$ , and carbon. Also effective are compact or supported nickel, tungsten, molybdenum, cobalt, and iron sulfides. The reaction is also promoted by aluminosilicate.<sup>10,69</sup>

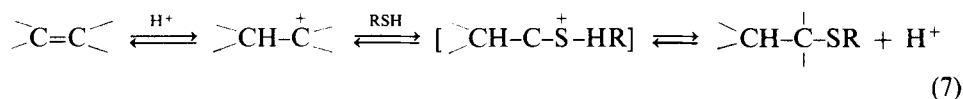
In the presence of solid catalysts the addition of  $H_2S$  to alkenes follows the Markovnikov rule. The process is promoted by increasing degree of alkene branching, pressure and alkene-to- $H_2S$  ratio. Under certain conditions a quantitative yield of the sulfide can be obtained.

Apparently, the formation of the dialkyl sulfide follows a consecutive mechanism via thiol formation:



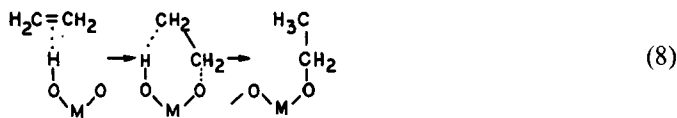
since the addition of a thiol to an alkene to form a sulfide is activated by the same catalysts as alkene thiolation with  $H_2S$ .<sup>8</sup> It has been noted<sup>8,69</sup> that the sulfide is obtained at higher temperatures than the thiol.

It has been suggested<sup>70</sup> that under the effect of proton centers of a solid catalyst the reaction takes place via the formation of a carbocation which interacts with  $H_2S$  or thiol:



where R is alkyl or H.

The view on the activation mechanism of alkenes can, however, be different.<sup>22,71</sup> Alkene interaction with acid hydroxyl groups first produces a complex with a hydrogen bond. Then the two-point adsorption of the alkene and its displacement to a neighboring basic centers take place, which results in the formation of a surface alkoxide:



On catalysts with Lewis acid centers the alkene forms a  $\pi$ -complex whose further conversion also yields a surface alkoxide. Interaction of alkoxide with  $\text{H}_2\text{S}$  or thiol produces the dialkyl sulfide according to the above Schemes 2–4 for thiol and sulfide synthesis from alcohols and  $\text{H}_2\text{S}$ .

### II.1.2. Synthesis of Dialkyl Sulfides from Alkanethiols

II.1.2.1. *Disproportionation of thiols to sulfides and  $\text{H}_2\text{S}$*  Decomposition of alkanethiols to sulfides and  $\text{H}_2\text{S}$  is thermodynamically possible, and this disproportionation reaction is reversible:



The equilibrium yield of the sulfide grows with decreasing temperature and molecular mass of the thiol (Table 8).

The disproportionation reaction takes only place in the presence of catalysts. Under the effect of  $\gamma\text{-Al}_2\text{O}_3$  at 370 and 410 °C and a contact time of 6 s methanethiols convert to dimethyl sulfides and  $\text{H}_2\text{S}$  in a yield close to the thermodynamically possible value.<sup>12</sup> In the presence of  $\text{Al}_2\text{O}_3$  or NaX zeolite at 100–400 °C ethanethiols decompose to diethyl sulfides and  $\text{H}_2\text{S}$ .<sup>72–76,80–89</sup>

Butanethiols activated by aluminosilicate are partially decomposed to yield sulfides whose formation rate grows in the sequence: normal > iso-secondary > tertiary sulfides. The reaction takes place at 350 °C and long (about 16 s) contact times. Therefore the main reaction is cracking of the thiols and the yield of sulfides is as high as 4 mol. %. Besides di-*n*-butyl sulfide, *n*-butanethiol gives a certain amount of ethyl *tert*-butyl sulfide. In addition to disproportionation, one can also observe isomerization of e.g. *n*-butanethiol to secondary and tertiary butanethiols. The selectivity towards sulfides slightly increases in the case of AlSi modified with sodium sulfide.<sup>77</sup> Interaction of methane- and ethanethiols with metal and oxide films of Al, Cu, Fe, Pd and Ni at

**Table 8.** Equilibrium conversion depths for thiols in the reaction  $2 \text{RSH} \rightleftharpoons \text{R}_2\text{S} + \text{H}_2\text{S}$ <sup>79</sup>

| T (K) | Equilibrium conversion depth (%) |                                 |                                 |
|-------|----------------------------------|---------------------------------|---------------------------------|
|       | $\text{CH}_3\text{SH}$           | $\text{C}_2\text{H}_5\text{SH}$ | $\text{C}_3\text{H}_7\text{SH}$ |
| 300   | 88                               | 87                              | 83                              |
| 400   | 80                               | 79                              | 74                              |
| 500   | 74                               | 73                              | 69                              |
| 600   | 70                               | 69                              | 65                              |
| 700   | 67                               | 66                              | 62                              |
| 800   | 65                               | 63                              | 60                              |
| 900   | 63                               | 62                              | 59                              |
| 1000  | 62                               | 61                              | 58                              |

67–127°C and long contact times produces sulfides. The reaction is accompanied by cracking of the thiols and the concentration of the sulfides in the mixture is low: 4–36 % and up to 2.5 % for methanethiol and ethanethiol conversion, respectively.<sup>78</sup>

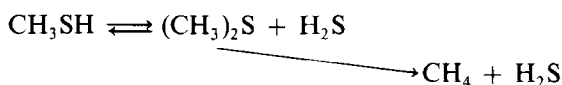
The most detailed study was carried out for methanethiol disproportionation catalyzed by various catalysts.<sup>79</sup> At constant temperature and initial concentration of thiol the yield of dimethyl sulfide from methanethiol grows with increasing contact time and reaches an equilibrium value (Table 9). On several catalysts ( $\text{Al}_2\text{O}_3$  without additives and modified by HF, HCl,  $\text{H}_2\text{SO}_4$  and Mo, Cr, Mg, Na, K, and Ti oxides) and also on HZSM-5 and SiW/SiO<sub>2</sub> at 200–350 °C, methanethiol destruction with elimination of hydrocarbon is not observed and the selectivity towards dimethyl sulfide is 100 %, even at the equilibrium extent of methanethiol conversion. At elevated temperatures, in addition to the formation of dimethyl sulfide, one can also observe the yield of methane to increase with increasing contact time. But even at 500 °C and 90 % of the equilibrium value of the conversion of thiol the selectivity towards the sulfide is 95 %. This high selectivity towards dimethyl sulfide was also found<sup>12</sup> in the disproportionation of methanethiol: at 90–95 % of the equilibrium value conversion (contact time 6 s) the selectivity of  $\text{Al}_2\text{O}_3$  towards dimethyl sulfide is equal to 99 and 95 % at 370 and 410 °C, respectively.

**Table 9.** The influence of the reaction conditions on the conversion of methanethiol to dimethyl sulfide<sup>79</sup>

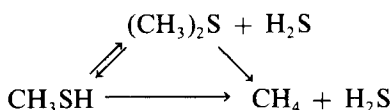
| Catalyst                                      | S<br>(m <sup>2</sup> /g) | T<br>(°C)               | CH <sub>3</sub> SH<br>(mmol/l) | τ<br>(s) | Dimethyl sulfide<br>Yield<br>(mol.%) | Selectivity<br>(%) |
|---|--------------------------|-------------------------|--------------------------------|----------|--------------------------------------|--------------------|
| $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ | 230                      | 200                     | 2.0                            | 0.71     | 22                                   | 100                |
|   |                          | 250                     | 2.0                            | 0.07     | 25                                   | 100                |
|   |                          | 250                     | 2.0                            | 0.14     | 50                                   | 100                |
|   |                          | 250                     | 2.0                            | 0.28     | 73                                   | 100                |
|   |                          | 350                     | 1.9                            | 0.01     | 44                                   | 100                |
|   |                          | 350                     | 1.9                            | 0.02     | 58                                   | 100                |
|   |                          | 350                     | 2.1                            | 0.14     | 68                                   | 99                 |
|   |                          | 400                     | 3.5                            | 0.02     | 55                                   | 100                |
|   |                          | 400                     | 3.5                            | 0.04     | 65                                   | 96                 |
|   |                          | 400                     | 3.2                            | 0.28     | 48                                   | 70                 |
|   |                          | 500                     | 16                             | 0.004    | 65                                   | 100                |
|   |                          | 500                     | 16                             | 0.19     | 63                                   | 94                 |
|   |                          | 500                     | 15                             | 0.40     | 50                                   | 70                 |
|   |                          | $\text{Al}_2\text{O}_3$ | 200                            | 225      | 1.8                                  | 0.43               |
| 225   | 2.0                      |                         |                                | 1.0      | 48                                   | 100                |
| 350   | 1.8                      |                         |                                | 0.006    | 30                                   | 100                |
| 350   | 2.0                      |                         |                                | 0.012    | 49                                   | 100                |
| AlSi  | 430                      | 350                     | 2.0                            | 0.66     | 7                                    | 100                |
|   |                          | 350                     | 2.0                            | 2.9      | 18                                   | 86                 |
|   |                          | 350                     | 2.0                            | 4.6      | 22                                   | 37                 |
| HNaY  | 800                      | 350                     | 1.9                            | 0.73     | 28                                   | 100                |
|   |                          | 350                     | 2.0                            | 3.6      | 22                                   | 40                 |
| $\text{Cr}_2\text{O}_3$                       | 330                      | 350                     | 2.0                            | 0.08     | 26                                   | 81                 |
|   |                          | 350                     | 2.0                            | 0.23     | 30                                   | 50                 |
|   |                          | 350                     | 2.2                            | 2.3      | 0                                    | 0                  |
| $\text{K}_2\text{WO}_4/\text{Al}_2\text{O}_3$ | 220                      | 250                     | 2.1                            | 1.2      | 40                                   | 100                |
|   |                          | 350                     | 2.2                            | 0.05     | 48                                   | 100                |
|   |                          | 350                     | 2.2                            | 0.16     | 63                                   | 100                |

The total conversion of methanethiol in the presence of various catalysts rises with temperature. One can observe a linear logarithmic dependence of the rate constant on  $1/T$ . For  $\text{Cr}/\text{Al}_2\text{O}_3$  the apparent activation energy is  $69 \text{ kJ/mol}$  and  $\lg K_0 = 8.5$ .

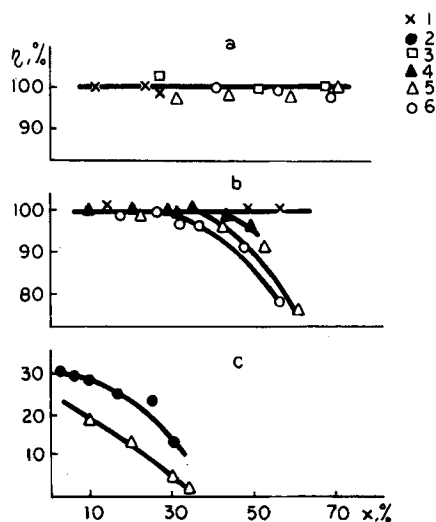
As it follows from the dependence of the selectivity towards the products of the conversion,<sup>79</sup> the decomposition of methanethiol on the above catalysts at  $150\text{--}500^\circ\text{C}$  follows a consecutive mechanism. It means that methanethiol disproportionates to  $\text{H}_2\text{S}$  and dimethyl sulfide at higher conversions obtained with increasing contact times. The sulfide formed decomposes to methane and  $\text{H}_2\text{S}$ :



In the presence of some catalysts ( $\text{HNaY}$ ,  $\text{NaX}$ ,  $\text{AlSi}$ ,  $\text{SiW}/\text{Al}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$ ) the disproportionation is accompanied by the formation of methane at low temperatures and far from equilibrium (Table 9, Figure 6). The reaction follows a parallel-consecutive mechanism:



The catalyst activity in the methanethiol disproportionation depends on the composition, in particular on the acid-base properties of the catalyst surface.<sup>79</sup> The experiments were carried out at  $350^\circ\text{C}$ ,  $1.8 \mu\text{mol/l}$  methanethiol in helium on  $0.25\text{--}0.5 \text{ mm}$  catalyst grains in the kinetic region. For each experiment a fresh catalyst sample was used which



**Figure 6.** The influence of thiol conversion on the selectivity towards dimethyl sulfide (a), diethyl sulfide (b) and diisopropyl sulfide (c) over  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  at the temperatures:  $200$  (1),  $225$  (2),  $250$  (3),  $320$  (4),  $350$  (5), and  $400^\circ\text{C}$  (6).<sup>79</sup>

**Table 10.** The activities of catalysts for the disproportionation of methanethiol to dimethyl sulfide and H<sub>2</sub>S at 350 °C<sup>79</sup>

| Catalyst  | Disproportionation rate, $v$<br>mmol/g·h | $\mu\text{mol}/\text{m}^2 \cdot \text{h}$ |
|---|--|---|
| SiO <sub>2</sub>  | 0.3                                      | 0.8                                       |
| 30% H <sub>3</sub> PO <sub>4</sub> /SiO <sub>2</sub>                | 0.3                                      | 3.0                                       |
| 25% SiW/SiO <sub>2</sub>  | 7.0                                      | 34  |
| 1% WO <sub>3</sub> /SiO <sub>2</sub>                                | 5.5                                      | 15  |
| 2.5% Cr <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>               | 4.3                                      | 12  |
| AlSi  | 1.2                                      | 3   |
| HNaY  | 6.0                                      | 8   |
| HZSM  | 300                                      | 600                                       |
| NaX   | 8  | 10  |
| NaY   | 0.2                                      | 0.3                                       |
| MgO   | 1.1                                      | 20  |
| Al <sub>2</sub> O <sub>3</sub>                                      | 750                                      | 3200                                      |
| 10% HCl/Al <sub>2</sub> O <sub>3</sub>                              | 400                                      | 2000                                      |
| 5% H <sub>2</sub> SO <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>   | 380                                      | 1900                                      |
| 3% HF/Al <sub>2</sub> O <sub>3</sub>                                | 325                                      | 1630                                      |
| 2.3% Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> | 540                                      | 2720                                      |
| 1.5% MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>               | 400                                      | 2000                                      |
| Al <sub>2</sub> O <sub>3</sub>                                      |  |   |
| 1% WO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>                  | 390                                      | 1850                                      |
| 0.25% NaOH/Al <sub>2</sub> O <sub>3</sub>                           | 87                                       | 400                                       |
| Al <sub>2</sub> O <sub>3</sub>                                      |  |   |
| 0.5% NaOH/Al <sub>2</sub> O <sub>3</sub>                            | 10                                       | 48  |
| Al <sub>2</sub> O <sub>3</sub>                                      |  |   |
| 2% NaOH/Al <sub>2</sub> O <sub>3</sub>                              | 2  | 10  |
| 2% K <sub>2</sub> WO <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>   | 14                                       | 70  |

had been presulfidized with H<sub>2</sub>S (4 vol. % H<sub>2</sub>S in helium) at 350 °C for 30 min. Exceptions were HNaY, AlSi, HZSM-5, H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> which were not sulfurized. The catalyst activity was estimated from the total rate of methanethiol conversion ( $v$  (mmol/h)) per 1 g or 1 m<sup>2</sup> catalyst and in several cases per one active surface center at the same methanethiol conversion. This was achieved by experiments with varying contact times. The selectivity ( $\eta$ , (%)) is equal to the ratio of product yield to thiol conversion.

The acid-base properties of the catalysts examined were determined by evaluation of the IR spectra of adsorbed test molecules (cf. p. 287 and Table 2).

The catalyst activities at  $T = 350$  °C and 20% methanethiol conversion (about 30% of its equilibrium value) are given in Table 10. As can be seen the activities depend on the acid-base characteristics of the catalysts.

SiO<sub>2</sub> whose surface contains only very weak proton-donor centers, is of low activity: 20% conversion is obtained at long (12 s) contact times, the selectivity towards dimethyl sulfide is 50%, and the reaction products contain methane. It is possible that a certain activity is associated with the fact that SiO<sub>2</sub> contains admixed Al and Fe elements acting as Lewis acid centers. The activity of one proton center of SiO<sub>2</sub> is low and amounts to 0.3  $\mu\text{mol}/\text{h}$ . Modification of SiO<sub>2</sub> with phosphoric acid leads to the appearance of stronger proton-donor centers whereas Lewis and basic centers are not observed. This catalyst has the same per weight activity as SiO<sub>2</sub>, but the activity of one of its proton centers (6  $\mu\text{mol}/\text{h}$ ) is an order of magnitude higher. Modification of SiO<sub>2</sub> with the

stronger acid  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  \* leads to the formation of strong proton-donor centers whose amount is  $1.5 \mu\text{mol}/\text{m}^2$ . Lewis acid centers cannot be detected,<sup>90</sup> but very weakly basic centers can be formed. Methanethiol decomposition catalyzed by  $\text{SiW}/\text{SiO}_2$  takes place with 100% selectivity towards dimethyl sulfide up to equilibrium yields of the sulfide. The catalyst activity per 1 g or  $1 \text{ m}^2$  surface is much higher than with  $\text{SiO}_2$  and  $\text{H}_3\text{PO}_4/\text{SiO}_2$ . The activity of one proton center equals  $23 \mu\text{mol}/\text{h}$ , which is also much higher. These results indicate that under the effect of proton-donor catalysts thiol disproportionation is smooth provided they contain strong proton-donor centers.

In the presence of  $\text{HNaY}$  zeolite whose surface has basic centers, a certain number of strong Lewis acid centers, and a large number of strong proton-donor centers, the weight rate is similar to that on  $\text{SiW}/\text{SiO}_2$ . The activity per unit surface is lower and that per the number of proton centers is practically the same. With long contact times on  $\text{HNaY}$  besides dimethyl sulfide methane is formed, apparently due to decomposition of methanethiol. Similar results are also obtained in the presence of amorphous  $\text{AlSi}$  whose surface has similar acid-base surface characteristics.

The high-silica zeolite  $\text{HZSM-5}$  contains a large number of strong proton-donor centers, moderately basic centers, and very strong Lewis acid centers. This catalyst has a very high activity per 1 g and  $1 \text{ m}^2$  surface. The activity of one proton center is two orders of magnitude higher than that to the above catalysts and equals  $2000 \mu\text{mol}/\text{h}$ . The disproportionation of methanethiol is very selective: at conversions equal to the equilibrium value the selectivity towards dimethyl sulfide is 100%. Apparently, the increased activity of  $\text{HZSM-5}$  is due to the fact that the surface of this catalyst contains very strong Lewis acid centers.

$\text{Al}_2\text{O}_3$  has a considerable concentration of strong Lewis acid and moderately basic centers, but no strong proton-donor centers. Its activity per 1 g or  $1 \text{ m}^2$  is considerably higher than that of  $\text{HZSM-5}$  with a lower concentration of strong Lewis acid centers. Hence it can be concluded that the rate of methanethiol disproportionation is so high due to the strong Lewis acid centers. If the catalyst contains insufficient amounts of strong Lewis acid centers, a decreased rate of thiol disproportionation to sulfide results. This can be exemplified by the 1.6%  $\text{Cr}/\text{SiO}_2$ , 1%  $\text{WS}_2/\text{SiO}_2$  catalysts with both strong proton-donor and Lewis acid centers with a strength lower than in  $\text{Al}_2\text{O}_3$  and hence the disproportionation rate is much lower than on  $\text{Al}_2\text{O}_3$  or  $\text{HZSM-5}$ . Low activities are also observed for other catalysts containing weak Lewis acid centers. For example, the rate of methanethiol disproportionation to dimethyl sulfide is low in the presence of  $\text{NaX}$  and  $\text{NaY}$  zeolites and of  $\text{MgO}$ . These catalysts contain no proton centers, but such centers can be generated during the reaction under the effect of alkanethiol or  $\text{H}_2\text{S}$  formed (cf. p. 285). They contain a considerable number of moderately basic centers and strong Lewis acid ones. The activity of  $\text{NaX}$  and  $\text{MgO}$  per unit surface is of the same order of magnitude. The lower activity of  $\text{NaY}$  is ascribed to the smaller number of non-localized sodium cations acting as Lewis acid centers in  $\text{Na}$  zeolites. Besides, as has already been noted, the basicity of  $\text{NaY}$  is lower compared to  $\text{NaX}$ ,  $\text{MgO}$ .

The necessity for the presence of not only strong acid centers but also of basic ones of sufficient strength is confirmed by the comparison of the activities of  $\text{Al}_2\text{O}_3$  catalysts unmodified and modified, respectively, by acid oxides ( $\text{Cr}_2\text{O}_3$ ,  $\text{MoO}_3$  and  $\text{WO}_3$ ) and

\*Silicotungstic acid is conventionally symbolized as  $\text{SiW}$ .

**Table 11.** The activity of NaOH/Al<sub>2</sub>O<sub>3</sub> catalysts in the disproportionation of methanethiol to dimethyl sulfide at 350 °C. The methanethiol conversion is 20% and its concentration 2 mmol/l<sup>79</sup>

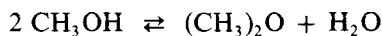
| Concentration of NaOH<br>in $\gamma$ -Al <sub>2</sub> O <sub>3</sub><br>(wt.%) |      | S,<br>(m <sup>2</sup> /g) | Contact<br>time<br>(s) | v/v <sub>0</sub><br>(%) | Strength of<br>Lewis acid<br>centers<br>Q <sub>CO</sub><br>(kJ/mol) |
|--|------|---------------------------|------------------------|-------------------------|---|
| 0  | 0    | 200                       | 0.0035                 | 100                     | 34  |
| 0.01   | 2.5  |                           | 0.0036                 | 97                      | 34  |
| 0.02   | 5.0  | 230                       | 0.0044                 | 80                      | 30  |
| 0.05   | 12.5 |                           | 0.005                  | 70                      | 29  |
| 0.1  | 25   | 207                       | 0.0085                 | 42                      | 29  |
| 0.25   | 62.5 |                           | 0.03                   | 12                      | 29  |
| 0.5  | 125  | 230                       | 0.25                   | 1.5                     | 29  |
| 1.0  | 250  |                           | 0.9                    | 0.4                     | 28  |
| 3.0  | 750  | 234                       | 1.6                    | 0.2                     | 26  |
| 5.0  | 1250 |                           | 2.9                    | 0.1                     | 18  |
| 10.0   | 2500 | 200                       | 5.0                    | 0.07                    | —   |

acids (HF, H<sub>2</sub>SO<sub>4</sub>, HCl). As seen from Table 10, the disproportionation rate of methanethiol is lower as compared to the initial Al<sub>2</sub>O<sub>3</sub>. Upon modification of Al<sub>2</sub>O<sub>3</sub> with acid additives there appear strong proton-donor centers and the concentration of Lewis acid centers decreases, but their strength increases slightly, basic centers with PA<sup>b</sup> = 800–900 kJ/mol are sharply suppressed, and there remain more weakly basic centers.

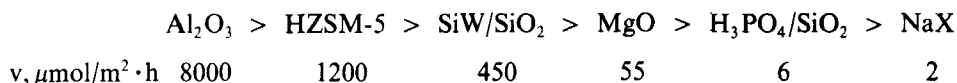
Alkaline and alkaline-earth additives to Al<sub>2</sub>O<sub>3</sub> suppress or destroy proton centers and diminish the concentration and strength of Lewis acid ones. On the surface there appear basic centers considerably stronger than in Al<sub>2</sub>O<sub>3</sub>. The catalyst activity decreases with increasing concentration of added alkali (Tables 10 and 11). A comparison of these results with the data for Al<sub>2</sub>O<sub>3</sub> modified by acids suggests that the presence of conjugated acid-basic pairs promotes sulfide formation from thiol. In this case the strength of the Lewis acid centers is more important than that of the basic ones.

Thus it can be concluded that the catalyst activity in the methanethiol disproportionation to dimethyl sulfide depends on the presence of conjugated acid-basic centers. The combination of basic with strong proton-donor centers is less favorable than their pairing with strong Lewis acid centers.

As it follows from the data for thiol adsorption on catalysts, the generated surface species are similar to those found for methanol adsorption (cf. p. 281). Experiments with methanol conversion on catalysts possessing different acid-basic properties showed that for the reaction



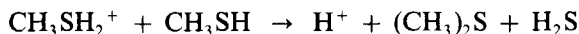
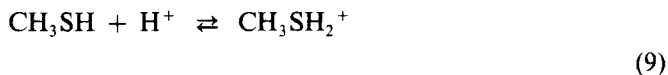
the catalyst activities follow the same sequence as for the methanethiol conversion at T = 350 °C (Table 10):





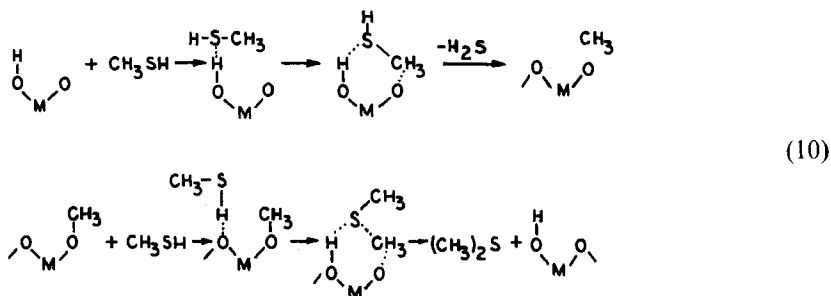
It can be suggested that the reaction mechanism for the methanethiol disproportionation is similar to that postulated for the alcohol decomposition.<sup>22,30</sup>

In the presence of catalysts only containing proton centers, e.g.,  $\text{H}_3\text{PO}_4/\text{SiO}_2$ , the reaction follows a carbocation mechanism:

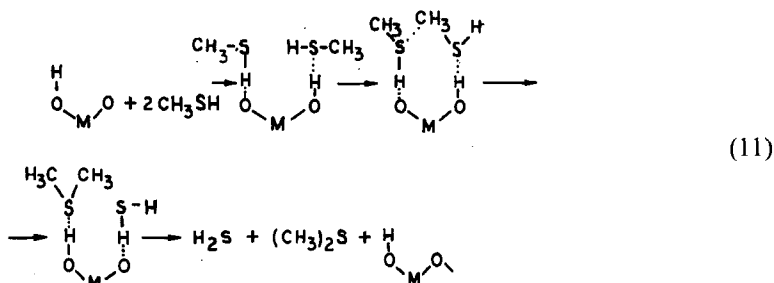


with the participation of methanethiol in the gas phase or weakly adsorbed on the catalyst.

When the reaction is catalyzed by catalysts with paired centers, under the effect of either preformed or reaction-generated proton centers, its first step will be thiol protonation which promotes the formation of an additional bond between alkyl and catalyst basic centers. Decomposition of the product complex to yield  $\text{H}_2\text{S}$  produces surface  $\text{CH}_3\text{O}$  species. During the second step  $\text{CH}_3\text{O}$  groups interact with a second thiol molecule adsorbed on the basic center. As a result sulfide is formed and the catalyst surface regenerated:



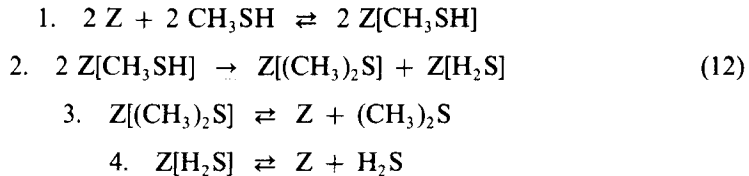
Apparently, the sulfide formation can also follow a concerted mechanism involving simultaneous activation and regeneration of several chemical bonds in the adsorbed molecule:



The participation of proton centers in methanethiol activation is confirmed by the sharp decrease of  $\text{Al}_2\text{O}_3$  activity upon after modification with very small quantities of sodium where only proton surface centers are blocked (Table 11). The preliminary

treatment of  $\text{Al}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  with  $\text{H}_2\text{S}$  or methanethiol at  $450^\circ\text{C}$  for 30 min increases their activity by a factor of 3–6 over the initial activity.

Kinetic studies of the reaction on  $\text{Al}_2\text{O}_3$  catalysts show that the rate of methanethiol decomposition to dimethyl sulfide and  $\text{H}_2\text{S}$  at low conversion degrees of thiol is described by an equation of pseudo-first order with respect to thiol, since the effect of variations of the thiol concentration (2–20 mmol/l) on the conversion is small and there exists a linear logarithmic dependence of  $\ln I/I - X$  on  $\tau$  ( $X$  = conversion,  $\tau$  = contact time). The reaction is assumed to involve the following elementary steps:



with a rate of limiting decomposition of the surface complex (step 2). In a general form the reaction is described by the equation:

$$v = \frac{K \cdot P_{\text{CH}_3\text{SH}}^2}{(1 + b_1 P_{\text{CH}_3\text{SH}} + b_2 P_{(\text{CH}_3)_2\text{S}} + b_3 P_{\text{H}_2\text{S}})^2}$$

As follows from the experimental data the inhibiting effect is produced only by methanethiol, hence the above equations reduces to

$$v = \frac{K \cdot P_{\text{CH}_3\text{SH}}^2}{(1 + b \cdot P_{\text{CH}_3\text{SH}})^2}$$

and at low conversions of methanethiol it transforms into a first-order equation:

$$v = K \cdot P_{\text{CH}_3\text{SH}}$$

At high conversions, one should take into account that the process is reversible.

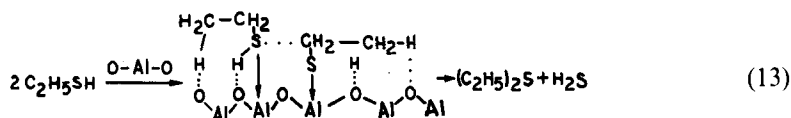
This disproportionation reaction also takes place with methanethiol homologs.

Ethanethiol disproportionation to diethyl sulfide and  $\text{H}_2\text{S}$  at  $50\text{--}400^\circ\text{C}$  is catalyzed by  $\text{Al}_2\text{O}_3$  and  $\text{NaX}$ . In the presence of  $\text{H}_3\text{PO}_4$ ,  $\text{AlSi}$ , and  $\text{HNaY}$  catalysts and cation forms of zeolites, one can observe only ethanethiol decomposition to ethylene and  $\text{H}_2\text{S}$ . On  $\text{SiO}_2$ ,  $\text{MgO}$ , and  $\text{CaO}$  ethanethiol undergoes no conversion.<sup>72–76,83–89</sup> From the dependence of the yield on the contact time at  $200\text{--}450^\circ\text{C}$  it has been concluded that ethanethiol conversion follows two different routes. It produces diethyl sulfide and  $\text{H}_2\text{S}$  as well as ethylene and  $\text{H}_2\text{S}$  are eliminated.

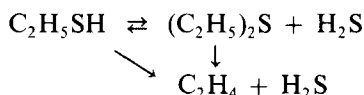
IR spectroscopic studies of ethanethiol adsorption<sup>73,75,76,86,87</sup> show that on  $\text{SiO}_2$ ,  $\text{CaO}$ , and  $\text{NaY}$  at  $20\text{--}50^\circ\text{C}$  only reversible adsorption takes place. On  $\text{Al}_2\text{O}_3$ ,  $\text{HY}$ ,  $\text{CoY}$ , and  $\text{ZnY}$  ethanethiol adsorption at room temperature leads to a broadening of OH vibration bands due to hydrogen bond formation and the appearance of new OH groups. The spectra exhibit bands corresponding to alkyl groups ( $\sim 2950$ ,  $1450$ , and  $1380\text{ cm}^{-1}$ ) and a band typical for the  $-\text{CH}_2-\text{S}-\text{M}$  structure ( $\sim 1260\text{ cm}^{-1}$ ), but there are no bands assignable to SH groups ( $\sim 2560\text{ cm}^{-1}$ ). At adsorption temperatures above  $50^\circ\text{C}$  there appear bands corresponding to  $\text{CH}_2-\text{CH}_2$  groups which are, apparently, responsible for the decomposition to ethylene. Desorption products of ethanethiol adsorbed on  $\text{Al}_2\text{O}_3$

contain ethanethiol as the main constituent at desorption temperatures 200–250 °C. At higher desorption temperatures, besides ethanethiol, the products contain considerable quantities of ethylene and H<sub>2</sub>S. It has been noted that the IR spectra of Al<sub>2</sub>O<sub>3</sub> acid centers adsorbed ethanethiol and diethyl sulfide are similar.

It is suggested that on Al<sub>2</sub>O<sub>3</sub> and NaX, acid-basic pairs of acid centers (Al<sup>3+</sup> or Na<sup>+</sup> cations) and basic centers (O<sup>2-</sup> or OH<sup>-</sup>) take part in the disproportionation of ethanethiol. The participation of basic centers is confirmed by the decrease of disproportionation after addition of phenol. The reaction follows the scheme:



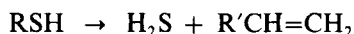
More detailed kinetic studies<sup>79</sup> of ethanethiol conversion catalyzed by Al<sub>2</sub>O<sub>3</sub> shows (Figure 6) that under certain conditions only ethanethiol disproportionation takes place and no formation of ethylene. For example, at 280–350 °C 100% selectivity towards diethyl sulfide is observed at 30–35% conversion of ethanethiol, i.e. 50% of the equilibrium value. At high conversion degrees the diethyl sulfide formed decomposes to yield ethylene and H<sub>2</sub>S. Kinetic curves of selectivity towards products (Figure 6) suggest that ethanethiol conversion follows a consecutive mechanism. At high temperatures some ethylene and H<sub>2</sub>S is obtained due to ethanethiol decomposition. Thus, the total scheme of the decomposition can be represented as



In the presence of Al<sub>2</sub>O<sub>3</sub>, NaX at 400 °C and Al, Ni, Cr, Co, or Fe fluoride 2-propanethiol decomposes only to propylene and H<sub>2</sub>S.<sup>73,74,88</sup> At lower temperatures a limited disproportionation to diisopropyl sulfide and H<sub>2</sub>S is observed,<sup>79</sup> but with low selectivity. For example, at 225 °C and a thiol conversion below 25% the selectivity is as high as 30%. With increasing reaction temperature, however, the selectivity towards the sulfide drops sharply (cf., e.g., Figure 6).

Decomposition to the alkene can be observed for both the initial thiol and for the sulfide formed by disproportionation. Some characteristic properties of these reactions are considered below.

*II.1.2.2. Catalytic decomposition of alkanethiols* The decomposition of thiols to yield alkenes and H<sub>2</sub>S:

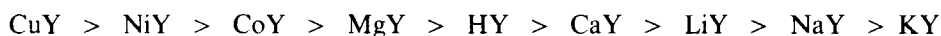


is thermodynamically possible in a wide temperature range.<sup>92</sup>

The reaction occurs without catalysts at above 400 °C (with *t*-butanethiol at 250 °C). Its rate increases with diminishing strength of the C–S bond in the starting thiol.<sup>82,92,93</sup> The process is accelerated in the presence of various catalysts containing proton centers (H<sub>3</sub>PO<sub>4</sub>, AlSi, and HNAY)<sup>72,74,82,85,87,89</sup> and Lewis acid centers (Al<sub>2</sub>O<sub>3</sub>, phosphates, fluo-

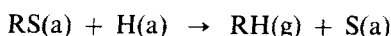
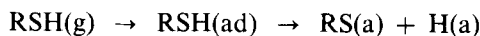
rides, sulfates, and cation forms of zeolites).<sup>72-76,83,87-89</sup> Basic catalysts (CaO and MgO) or catalysts containing weak proton-donor centers (SiO<sub>2</sub>) do not affect the decomposition of thiols to any appreciable extent.<sup>72,74,87</sup>

The activity of proton-donor catalysts in the decomposition of thiols depends on the concentration of surface proton centers a decrease of which (due to, e.g., increasing catalyst calcination temperature, catalyst modification with alkalis, or introduction of pyridine into the reaction mixture) diminishes the reaction rate.<sup>72,88</sup> On AlSi a linear logarithmic dependence between the rate constant for the elimination of thiols with R = C<sub>2</sub>, C<sub>3</sub>, *i*-C<sub>3</sub>, C<sub>4</sub>, *s*-C<sub>4</sub>) and the enthalpy change of the hydride ion abstraction from the corresponding alkanes was observed.<sup>82</sup> This suggests that the reaction follows a carbocation mechanism through an easily occurring surface proton addition to the sulfur atom of the thiol, a slow decomposition of RSH<sub>2</sub><sup>+</sup> to the carbocation (RSH<sub>2</sub><sup>+</sup> → R<sup>+</sup> + H<sub>2</sub>S), and fast interaction of the latter with an anion to yield an alkene and H<sup>+</sup>:R<sup>+</sup> + A<sup>-</sup> ⇌ (R-H) + H<sup>+</sup> A<sup>-</sup> - AlSi, (R-H) is an alkene). The activity of NaY zeolites at 350 °C in the decomposition of butanethiol to butene and H<sub>2</sub>S<sup>94</sup> rises by a factor of 7 with increasing decationation degree of zeolites (from 7 to 80%), which points to an important role of proton centers. But it is likely that the decomposition of thiols is also assisted by Lewis acid centers since the elimination of butene from butanethiol also takes place in the presence of zeolites in various cation forms.<sup>94</sup> It has been found that zeolites with 60% decationation fall into the following activity sequence:

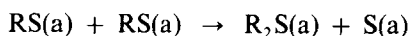


The difference between the first and the last member of this sequence is larger than two orders in magnitude. This sequence corresponds to the increase in the acceptor functions of cations. At 450–500 °C butanethiol decomposes to hydrocarbons and H<sub>2</sub>S under the effect of oxides and sulfides of period 3–6 elements. The catalyst activity is determined by the acceptor properties of the cations. In the presence of several catalysts thiol decomposition to hydrocarbons and H<sub>2</sub>S is accompanied by a parallel cyclization to thiophene.<sup>95,96</sup>

The activity of the sodium forms of X and Y faujesite in the elimination of ethylene and H<sub>2</sub>S from ethanethiol in a methane medium at 350 °C and P = 0.6 MPa is 2–5 times higher than that of decationated forms, and the reaction is assumed to follow a radical mechanism.<sup>66</sup> C<sub>1</sub>–C<sub>3</sub> thiols decompose to yield hydrocarbons and H<sub>2</sub>S in their interaction with metal and oxide films of Fe, Pd, Ni, Al, Cu, and W already at –80 °C. With increasing temperature their decomposition rate rises. It is suggested that on metal films thiols decompose by cleavage of the S–H bond to form RS<sup>·</sup> and H<sup>·</sup> radicals. On oxide films the dissociation takes place with the dissociation of one more bond, the C–S bond, to form RS, SH, OH, and R radicals. The formation of hydrocarbons takes place via the reactions:

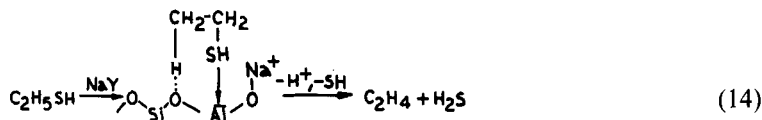


The interactions of RS structures produces sulfides

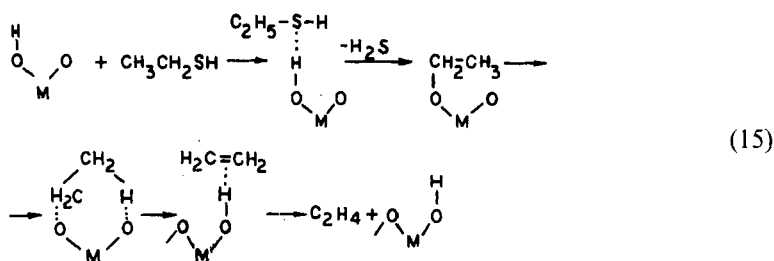


The reversibility of the thiol conversion to sulfides has not been established.<sup>78</sup>

The reaction mechanism for thiol decomposition involving the participation of cations is evidenced by studies of the activity of metal-containing zeolites and also of some metal phosphates and fluorides as well as  $\text{Al}_2\text{O}_3$ .<sup>72,73,83,88,89</sup> For MeY zeolites (Me = Ni, Co, Zn, Cd, Cu, Ag, Pb, Mn, Al, Ba, Cr, Mg, Na, and Fe) the catalytic activity in ethylene elimination from ethanethiol depends on the electronegativity of the cations in the catalysts. For ethanethiol the reaction is suggested<sup>83</sup> to follow the scheme:

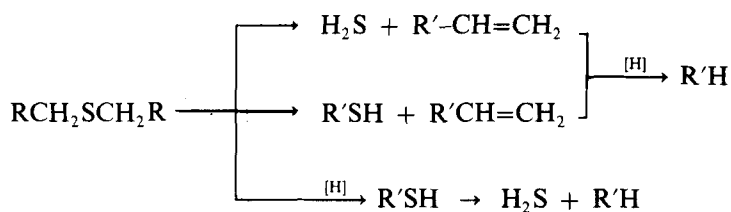


But is it possible that the ethylene elimination from ethanethiol takes place, similar to ethanol dehydration,<sup>22</sup> via formation of ethoxyl groups and their further conversion:



*II.1.2.3. Catalytic decomposition of dialkyl sulfides* It is thermodynamically probable that the conversion of dialkyl sulfides follows two routes: the formation of thiols or alkenes or of  $\text{H}_2\text{S}$  and alkenes.<sup>92</sup> Sulfide dissociation via the former route is less probable than via the latter, for which the equilibrium of sulfide dissociation at 600–700 K is close to 100%. The former reaction route is favored by decreasing temperature.<sup>92,97–99</sup>

The decomposition of dialkyl sulfides in the presence of amorphous AlSi zeolites has been studied in detail.<sup>77,92,97–100</sup> The decomposition of sulfides with unbranched ( $\text{C}_3$ – $\text{C}_9$ ) or branched chains ( $\text{C}_4$ – $\text{C}_9$ ) where the sulfur atom is linked to either a primary or a secondary carbon atom has been studied in the presence of AlSi.<sup>97,98</sup> The degree of sulfide decomposition increases with increasing temperature, contact time, and molecular weight. The reaction rate depends on the sulfide structure. It is highest for the sulfides whose sulfur atom is linked to a secondary carbon atom. Higher conversion rates are observed for branched sulfides than for unbranched ones. Considerable amounts of thiols are obtained at 200–300 °C and 60–80% sulfide conversion the selectivity towards thiol equals 80–90% with 50–70% yield of thiols. At higher temperatures noticeable amounts of alkenes and  $\text{H}_2\text{S}$  are formed. Sulfides also decompose to yield hydrogen which can take part in the hydrogenolysis of thiols and sulfides. Kinetic data suggest the following mechanism for the formation of the reaction products:



In the case of the conversion of sulfides whose sulfur atoms are linked to secondary carbon atoms the primary product is a thiol and its decomposition in turn produces alkenes and  $\text{H}_2\text{S}$ . When the reaction involves the participation of sulfides whose sulfur atom is linked to primary carbon atoms the formation of thiols and the decomposition of sulfides to  $\text{H}_2\text{S}$  and olefins take place independently. At higher temperatures and longer contact times thiols also decompose to  $\text{H}_2\text{S}$  and alkenes. In the presence of AlSi at 250–400 °C the conversion of dibutyl sulfide follows a parallel-consecutive scheme.<sup>77</sup> At 200–300 °C by and large two independent reactions yield thiols and  $\text{H}_2\text{S}$ , respectively. At higher temperatures the process becomes more complicated. The selectivity towards thiols rises with increasing temperature and decreasing conversion degree of sulfides: at 70% conversion the selectivity towards butanethiol equals 87% at 300–350 °C and is only 32% at 400 °C. AlSi modification with sodium sulfide diminishes the conversion degree of sulfides. In this case the yield of both thiols and  $\text{H}_2\text{S}$  decreases, whereas the selectivity towards thiols remains practically unchanged.

In the presence of NaA, NaX, and NaY zeolites and amorphous AlSi, dipropyl sulfide decomposition has been studied<sup>100</sup> at 250–450 °C and a contact time of 30–40 s. With increasing temperature the thiol yield increases, the selectivity towards the thiol decreases and the products contain gaseous  $\text{C}_3$  and low amounts of  $\text{C}_1$ – $\text{C}_2$ . The catalyst is covered by sulfur and coke. The maximum yield of propanethiol (70%) was obtained on MgNaY with 22% exchange. The catalyst is stable for 40 h of continuous operation and after deactivation it can be regenerated. The sulfide conversion to thiols at 250 °C on this catalyst rises from 45 to 65% when going from  $\text{C}_2$  to  $\text{C}_6$ . Its selectivity is 84–88%.

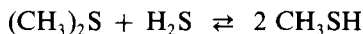
Dimethyl sulfide conversion is more difficult.<sup>91,101</sup> In the presence of  $\text{Al}_2\text{O}_3$  at 400–500 °C, atmospheric pressure, 30–45 vol.% concentration of sulfide in helium, and contact times of 0.6–10.0 s dimethyl sulfide decomposition produces methanethiol,  $\text{H}_2\text{S}$ , methane, and small quantities of  $\text{C}_2$  hydrocarbons. The decomposition rate rises with increasing temperature, contact time, and dimethyl sulfide concentration. The selectivity towards the thiol drops as the conversion degree rises, which indicates further conversion of the methanethiol formed. The maximum yield of methanethiol is 23 mol.% and the selectivity 37%. At 16% conversion the maximum selectivity towards methanethiol is 63%. It is possible that the decomposition of sulfides and thiols to form methane is aided by hydrogen arising from their extensive cracking. As the duration of the experiments increases both the total dimethyl sulfide conversion and the yield of products drop, but the selectivity towards the thiol changes only slightly. The process is first order with respect to dimethyl sulfide. The catalyst stability characterized by the time required for the initial concentration to decrease by 50%, diminishes with increasing temperature and sulfide concentration and with decreasing contact time. This implies that the catalyst deactivation is largely caused by the decomposition of the sulfide rather than by that of its conversion products.

The catalyst surface becomes covered with sulfur, but this does not affect its activity. Carbon accumulation on the catalysts in excess of 10 wt. % leads to a drop of their initial activity. The concentration of the coke deposited grows with increasing conversion of the dimethyl sulfide.

Electron microscopic and EPR studies of coke formation on  $\gamma\text{-Al}_2\text{O}_3$ <sup>102</sup> show that at small surface coverages by carbon the condensation degree of the coke is low, but rises with the coke concentration. In the process of coke deposition the accessible catalyst surface decreases and its active sites are blocked. It is possible that the coke deposit contains sulfur but the sulfur does not enter into the conjugated system of the polymeric carbon structure and is localized in its peripheric aliphatic part. This conclusion was made in accordance with the fact that the *g*-factor in the EPR spectra of coke deposits is close to that of a free electron. Apparently, the surface of alumina like that of other oxides, can contain strongly adsorbed sulfur-containing structures produced by chemisorption of  $\text{H}_2\text{S}$ , dimethyl sulfide, and methanethiol, e.g.,  $\text{SH}^-$ ,  $\text{CH}_3\text{S}^-$ ,  $\text{S}$  and  $\text{CH}_3\text{SO}_x^-$ . Electron microscopic data indicate that the amorphous deposits cover some isolated crystallites of  $\gamma\text{-Al}_2\text{O}_3$  at low concentrations of coke. When its concentration grows the coke deposits connect the  $\gamma\text{-Al}_2\text{O}_3$  crystallites. EPR studies revealed that at low concentrations (below 13 wt. %) of coke it has a low-condensed structure and the catalysts pores are open. As the concentration of the coke deposited on the catalyst rises, its degree of condensation grows and the separate agglomerates merge to form a monolithic coverage.

Thus the main reason for the catalyst deactivation in dimethyl sulfide decomposition in inert media under the effect of  $\gamma\text{-Al}_2\text{O}_3$  at  $T = 400\text{--}500^\circ\text{C}$  and atmospheric pressure is carbon deposition on the catalyst surface. Deactivated catalysts can be regenerated by treatment with air at  $500\text{--}550^\circ\text{C}$ . The regeneration is easier with samples containing low-condensed coke on their surfaces.

The decomposition of dimethyl sulfide to methane is sharply inhibited by added  $\text{H}_2\text{S}$ , since in this case the predominant reaction becomes disproportionation:<sup>104</sup>



This reaction is accelerated by acid type catalysts: unmodified  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  modified with Cr, Mo, Co, and W oxides and sulfides, phosphoric and phosphorotungstic acid, zeolites, and phosphates. In the presence of  $\text{Al}_2\text{O}_3$  modified with NaOH or KOH the reaction rate is low (at  $280\text{--}370^\circ\text{C}$  and molar ratio  $\text{H}_2\text{S}:(\text{CH}_3)_2\text{S} = 1.5\text{--}2.0$ ) compared to unpromoted  $\text{Al}_2\text{O}_3$  and 2–100 times lower as the alkali concentration increases from 0.1 to 2.5 wt. %. These catalysts contain strongly basic and sharply inhibited Lewis acid centers. Catalysts containing largely strong proton-donor centers (40 wt. % phosphorotungstic acid on  $\text{SiO}_2$ , AlSi, and HNaY) are more active compared to the former. The highest activity is observed for aluminium oxide catalysts: unmodified  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  modified by acid additives (0.3–3.0 wt. % HF, 3 wt. %  $\text{H}_2\text{SO}_4$ , and 5 wt. %  $\text{WS}_3$ ). In the presence of alumina catalysts with approximately the same concentrations of Lewis acid centers the rate of methanethiol formation increases with the strength of the Lewis acid centers. IR spectroscopic studies show that treatment of  $\text{Al}_2\text{O}_3$  or HF/ $\text{Al}_2\text{O}_3$  catalysts with dimethyl sulfide leads to a complete blocking of Lewis acid centers as detected by the CO adsorption method (cf. p. 287). This supports the assumption that dimethyl sulfide conversion in the presence of  $\text{H}_2\text{S}$  is affected by Lewis acid centers.

the reaction is reversible its mechanism is likely to be similar to that of the above-mentioned disproportionation of alkanethiols to dialkyl sulfide and  $\text{H}_2\text{S}$ .

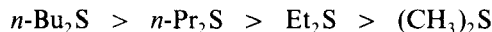
In the absence of  $\text{H}_2\text{S}$ , at 400–500 °C the disproportionation of dimethyl sulfide homologs to hydrocarbons and  $\text{H}_2\text{S}$  readily takes place under the effect of various catalysts.

Diethyl sulfide decomposition<sup>105</sup> is promoted by proton-donor catalysts: aluminum, magnesium, and zirconium silicate and  $\text{SiO}_2$  either unmodified or promoted by phosphoric acid. According to the activity of one proton center at 500 °C the catalysts can be arranged in the following sequence:

|                         |   |               |   |               |   |                                      |   |                |  |       |
|-------------------------|---|---------------|---|---------------|---|--------------------------------------|---|----------------|--|-------|
| $\text{AlSi}$           | > | $\text{ZrSi}$ | > | $\text{MgSi}$ | > | $\text{H}_3\text{PO}_4/\text{SiO}_2$ | > | $\text{SiO}_2$ |  |       |
| $k_{\text{H}^+}$ , ml/s |   | 0.5           |   | 0.4           |   | 0.25                                 |   | 0.1            |  | ~0.01 |

The same sequence is observed for the decrease in the strength of the proton-donor centers of the catalysts. These results show that proton centers do take part in sulfide decompositions.

It is suggested<sup>80,81</sup> that on  $\text{AlSi}$  the decomposition of sulfides occurs via formation of  $\text{R}_2\text{SH}^+$  and its further conversion to  $\text{R}^+$  and thiol, which in turn undergo further decomposition. The fact that the reaction involves sulfide protonation can be argued<sup>72,80,83</sup> by the activity decrease of  $\text{AlSi}$  modified by alkalis. For example, the addition of about 1 wt. %  $\text{KOH}$  to  $\text{AlSi}$  decreases the rate constant of diethyl sulfide decomposition by 50%. There is a linear logarithmic dependence of the rate constant on values characterizing enthalpy changes for hydride ion abstraction from the corresponding alkene. According to their reactivities in the decomposition at 200–350 °C on  $\text{AlSi}$  and at 400 °C on  $\text{H}_3\text{PO}_4$ , dialkyl sulfides can be arranged in the sequence:



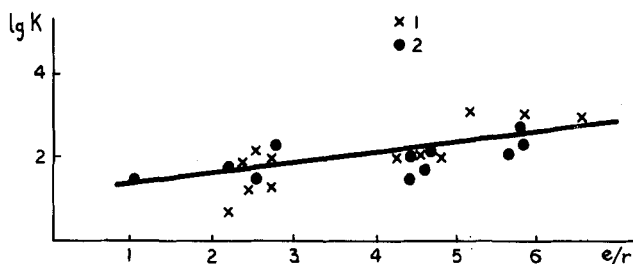
corresponding to the basicities of the sulfide sulfur atoms.

At the same time, catalysts with acceptor centers only, e.g.,  $\text{Al}_2\text{O}_3$  unmodified or modified by alkalis, are more active in the decomposition of sulfides to hydrocarbons and  $\text{H}_2\text{S}$ . A number of clues indicate that the reaction takes place through the formation of a donor-acceptor complex with the participation of a sulfide sulfur atom and a cation. The extent of charge transfer from the sulfur atom to aluminum in  $\text{AlBr}_3$  and the strength of the  $\text{Al-S}$  bond are higher than the corresponding values for  $\text{TiCl}_4$ . For example, the dipole moments for the complexes of dialkyl sulfides with  $\text{AlBr}_3$  equal 7.08 Debye and their formation heat is 74 kJ/mol. In solutions containing  $\text{AlCl}_3$  the decomposition of sulfides is more rapid than in the presence of e.g.,  $\text{SnCl}_4$  or  $\text{ZrCl}_2$ . The catalytic activity of  $\text{Al}_2\text{O}_3$  in the decomposition of diethyl sulfide at 500 °C is 75 times higher than that of  $\text{TiO}_2$ .

The consideration<sup>105</sup> of stability trends for complexes with sulfur-containing ligands such as methionine, cysteine and *o*-(ethylthio)benzoic acid, shows that although the complex stability depends on the nature of the ligand, the order of its variations for each sequence remains approximately unchanged. The activity of metal oxides or sulfides in the decomposition of dialkyl sulfides varies approximately in the same sequence as the complex stabilities.

There is a correlation between catalytic activities and stability constants for the other





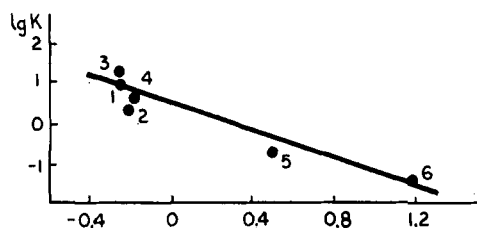
**Figure 7.** Quantitative correlation of the logarithmic rate constants for diethyl sulfide decomposition at 500 °C ( $K \cdot 10^3 \text{ ml/m}^2 \cdot \text{s}$ ) with  $e/r$  values over metal oxides (1) and sulfides (2).<sup>105</sup>

complexes as well. The activity of the catalysts examined changes symbatically with the charge to radius ratio  $e/r$  of the cations and also with the symbatically associated ionization potentials and electron affinities of the metal ions. This correlation exists irrespective of the fact that neither metal oxides nor sulfides are used as catalysts (Figure 7).

When the activities of the catalysts are quantitatively correlated with the  $e/r$  values it appears that the correlation coefficient is 0.63, the dispersion of the empirical correlation coefficient 0.12, and the root-mean-square deviation from the regression line 0.08. With no less than 0.99 probability it can be stated that a correlation between  $\lg K$  and  $e/r$  exists. A similar correlation has also been established for the decomposition of dibutyl sulfides to  $\text{H}_2\text{S}$  and hydrocarbons. This correlation implies that the catalyst activity is mainly due to the acceptor activity of the cations entering in the catalyst.

A symbatic dependence is also observed between the activities of catalysts in elimination reactions and the electronegativity difference between metals and oxygen or sulfur which characterizes to a first approximation the ionic character of the metal-chalcogen bond, and also on the metal–non-metal distance in the crystal lattice of the catalyst. This can be ascribed to the fact that the above properties go parallel with the acceptor strength of the cation.

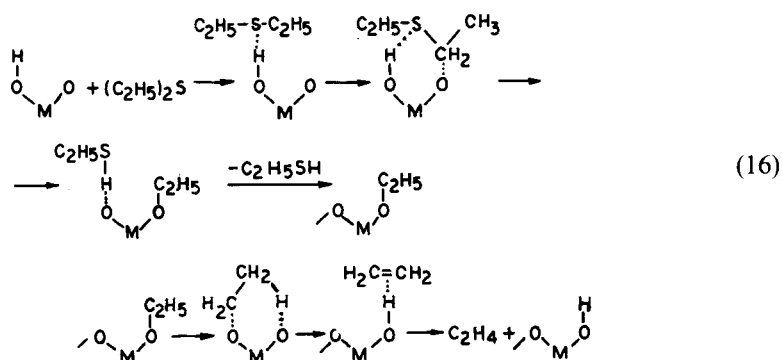
The reactivities of sulfides with different structures and the conversion on this catalyst are determined by their donor strengths (Figure 8). This also confirms the suggested mechanism implying that the reaction takes place via the formation of a donor-acceptor complex whose reactivity depends on both the Lewis acidity of the cation and the donor strength of the sulfide sulfur atom.<sup>106</sup>



**Figure 8.** The logarithmic dependence of the rate constants for sulfide decomposition at 300 °C over  $\gamma\text{-Al}_2\text{O}_3$  on the inductive constants in Taft's equation. 1 — diethyl; 2 — ethyl butyl; 3 — diisomyl; 4 — di-*n*-octyl; 5 — ethyl phenyl, and 6 — diphenyl sulfide.<sup>204</sup>

Another important feature is, apparently, the presence in the catalyst of not only acceptor centers but also associated basic ones. This can be seen e.g. by comparison of  $\text{Al}_2\text{O}_3$  and  $\text{HF}/\text{Al}_2\text{O}_3$  catalysts. The fluorinated sample has strong Lewis acid centers, but is of low basicity and its activity is an order of magnitude lower than that of  $\text{Al}_2\text{O}_3$ .

Studies of the adsorption of dialkyl sulfides on catalysts show that the dissociative adsorption of sulfides produces structures of the same type as those formed in the adsorption of methanethiol and dimethyl sulfides (cf. p. 286). It can be assumed that the decomposition of sulfides yielding thiols,  $\text{H}_2\text{S}$ , and alkenes takes place under the effect of conjugated acid-base pairs of centers similar to the decomposition of thiols discussed above. Since a sulfur atom in a sulfide has a higher donor ability than that in a thiol the dissociative adsorption of sulfides with the dissociation of the C-S bond and with the formation of a surface alkoxy group and the formation of thiols is easier on these centers. Under certain conditions alkoxy groups decompose to yield alkenes and then the thiols decompose and produce  $\text{H}_2\text{S}$  and alkenes (*vide supra*). The decomposition of e.g. diethyl sulfide can be described by the scheme:



Elimination of alkenes and  $\text{H}_2\text{S}$  from thiols also takes place through the formation of an alkoxy group (cf. p. 314, Scheme 15). It is obvious that the formation of the above products can also take place during the simultaneous activation of the bonds in a sulfide molecule.

A generalization of the results given in Section II.1.2. suggests that the disproportionation of thiols to sulfides and  $\text{H}_2\text{S}$  and the decomposition of these compounds to alkenes take place with the aid of the same active centers of the catalysts. The direction of this process depends only on the reaction conditions. The disproportionation of thiols to sulfides is favored by decreasing temperatures and contact times, whereas the decomposition of thiols and dialkyl sulfides to yield hydrocarbons is favored by corresponding increases. The concentrations of the reactants affect the yields of the end products only to a limited extent.

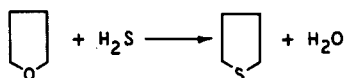
A comparison of the rates for the decomposition to hydrocarbons and  $\text{H}_2\text{S}$  of some thiols and dialkyl sulfides in the presence of aluminosilicate catalysts at the same temperature shows<sup>80-82</sup> that the rate constant of sulfide decomposition is one-two orders of magnitude higher than that for the decomposition of the corresponding thiols.

Apparently this is true for the other catalysts as well. The decomposition rates for thiols with branched structure are two orders of magnitude larger than for those with unbranched structures. Hence it can be suggested that in the case of sulfide formation from 1-alkanethiols a secondary reaction forming an alkene takes place largely from the sulfide, whereas in the case of secondary alkanethiols alkenes can be formed from both thiols and sulfides.

## II.2. Cyclic Sulfides

**II.2.1. Synthesis of thiolane from tetrahydrofuran and  $H_2S$**  Five-membered cyclic sulfides and their alkyl substituted derivatives can be obtained by exchange of oxygen, nitrogen, or selenium atoms in the ring by sulfur supplied as  $H_2S$  (Yuriev's reaction, 1936). Without catalysts no recyclization takes place and thus their presence is required in this reaction.

The most comprehensive studies have been carried with the formation of thiolane from tetrahydrofuran (THF) and  $H_2S$ .



Thermodynamic calculations show that at temperatures in the range 25–725 °C the equilibrium conversion of tetrahydrofuran to thiolane is 100%.

The recyclization processes are carried out in the presence of various catalysts at 25–450 °C. Yuriev *et al.*<sup>107–111</sup> applied  $Al_2O_3$  both unmodified and modified by chromia, thoria, and iron oxides. The patent literature<sup>112–115</sup> reports the use of alumina modified with aluminum and magnesium phosphate, silicic acid, phosphoro- and silicotungstate heteropolyacids and their potassium salts as catalysts. The application of HY, NaX, and NaY zeolites as catalysts has been suggested in.<sup>116,117</sup> A qualitative comparison of the activities of the above catalysts is difficult since the synthetic conditions were different. Some rules for the selection of catalysts for thiolane synthesis from tetrahydrofuran and  $H_2S$  have been established<sup>118,119</sup> on the basis of detailed studies of this reaction in the presence of various catalysts.

The catalytic activity is characterized by the rate of the total decomposition of tetrahydrofuran per 1 g catalyst (“weight activity”) or per active center (“specific activity”). The selectivity is the ratio of thiolane yield to tetrahydrofuran conversion.

*Proton-donor catalysts*  $SiO_2$ ,  $H_3PO_4/SiO_2$ ,  $SiW/SiO_2$ , amorphous aluminosilicate (AlSi) and HNaY, HZSM zeolites accelerate the recyclization reactions. The yield of thiolane depends on the synthetic conditions and the catalyst composition (some data are given in Table 12).

At constant contact time and a temperature increase from 300 to 400 °C the conversion of tetrahydrofuran increases, the selectivity towards thiolane decreases, and the yield of thiolane changes only slightly, whereas that of  $C_3$ – $C_4$  hydrocarbons rises. In all experiments a great imbalance with respect to carbon (50–80%) is observed. The catalysts are unstable in the reaction. For example, at  $T = 360$  °C and  $\tau = 1$  s, as the reaction time on HZSM rises from 30 to 150 min, the conversion of tetrahydrofuran and

the yields of thiolane and hydrocarbons drop by a factor of 3–5, but the selectivity towards thiolane changes only slightly and equals about 20%. With increasing tetrahydrofuran concentration the catalyst stability decreases. After preliminary treatment of HZSM for 30 min with 4 vol.% THF in helium the initial activity in the reaction of tetrahydrofuran with H<sub>2</sub>S at 360 °C drops by approximately a factor of 20.

In the absence of H<sub>2</sub>S tetrahydrofuran decomposes and polymerizes under the effect of inorganic acids (HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, and heteropolyacids) in solution<sup>107,120,121</sup> or in the presence of proton-donor catalysts. e.g., AlSi.<sup>122–126</sup>

The reaction product, thiolane, also deactivates HZSM catalysts, but to a lesser degree than tetrahydrofuran. After preliminary treatment of HZSM at 360 °C for 30 min with 3 vol.% thiolane in helium the initial activity of the catalysts in the reaction of tetrahydrofuran with H<sub>2</sub>S at 360 °C decreases only 50%. It is known<sup>77,127</sup> that on catalysts with strong proton-donor centers, e.g., AlSi, at 250–400 °C thiolane decomposes to yield H<sub>2</sub>S, alkenes, and condensation products. The analysis of aluminosilicate deactivated during the reaction of tetrahydrofuran with H<sub>2</sub>S shows<sup>118,119</sup> that its surface contains resinous deposits with a ratio C:H = 1:2. GC-MS data for the product washed out from the surface with acetone show that they can be unsaturated organic compounds containing 4–6 carbon atoms and apparently 1 oxygen atom. Thus, the observed imbalance with respect to carbon in the reaction products and the low selectivity towards thiolane is associated with the decomposition of tetrahydrofuran and the partial decomposition of thiolane accompanied by the deposition of condensation products on the catalyst surface.

In the presence of all examined proton-donor catalysts at 360 °C and a ratio H<sub>2</sub>S:THF = 1:5 with increasing contact time the conversion of tetrahydrofuran and the yield of thiolane increases. The selectivity towards thiolane on the H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalyst is insignificant, that on HNaY is 50% and on the remaining catalysts it is 20–30% (Table 12). When the conversion of tetrahydrofuran is less than 60% the

**Table 12.** The influence of the contact time on tetrahydrofuran conversion in H<sub>2</sub>S medium at T = 360 °C, [H<sub>2</sub>S] = 12.5 mmol/l and [THF] = 2.5 mmol/l<sup>118,119</sup>

| Catalyst   | Contact time, s | Tetrahydrofuran conversion, % | Thiolane yield, mol.% | Selectivity towards thiolane, % |
|--|-----------------|-------------------------------|-----------------------|---------------------------------|
| SiO <sub>2</sub>                                     | 2.7             | 19                            | 4                     | 21                              |
|  | 4.9             | 38                            | 9                     | 24                              |
|  | 8.1             | 52                            | 12                    | 23                              |
|  | 8.1*            | 70                            | 12                    | 17                              |
| 30% H <sub>3</sub> PO <sub>4</sub> /SiO <sub>2</sub> | 0.7             | 17                            | 1                     | 6                               |
|  | 14.4            | 84                            | 0.8                   | 1                               |
| HZSM   | 0.2             | 13                            | 3                     | 23                              |
|  | 0.8             | 54                            | 11                    | 20                              |
|  | 1.3             | 93                            | 17                    | 18                              |
|  | 0.1**           | 39                            | 7                     | 18                              |
| AlSi   | 0.4             | 29                            | 8                     | 28                              |
|  | 1.2             | 65                            | 12                    | 18                              |

\*T = 395 °C; \*\*T = 410 °C.

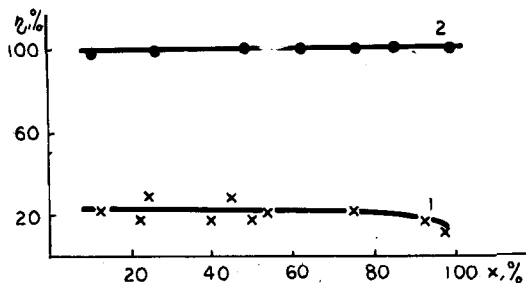
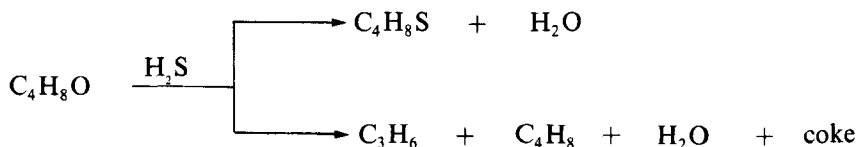


Figure 9. The selectivity towards thiolane vs. tetrahydrofuran conversion at 360 °C,  $\text{H}_2\text{S}:\text{C}_4\text{H}_8\text{O} = 5$  over HZSM (1) and  $\gamma\text{-Al}_2\text{O}_3$  (2).<sup>118</sup>

selectivity towards thiolane and hydrocarbons remains unchanged, which shows that the recyclization and the decomposition of tetrahydrofuran follow independent routes. At higher conversions of tetrahydrofuran the selectivity towards thiolane decreases because of decomposition (Figure 9):



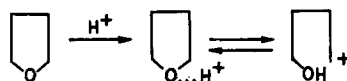
The experimental results at low conversions of tetrahydrofuran on catalysts with proton-donor centers can be described by a pseudo-first order equation with respect to tetrahydrofuran. The scattering of the rate constants for the first-order reaction calculated for various contact times is as high as 20 rel.%. One-parametric experiments in the presence of HZSM under gradientless conditions show that at a constant-flow concentration of  $\text{H}_2\text{S}$  (14 mmol/l) and with 1.4–8.0 mmol/l variation of the tetrahydrofuran concentration the total reaction rate remains practically unchanged, i.e. the order with respect to tetrahydrofuran is zero. At a constant-flow concentration of tetrahydrofuran (3 mmol/l) and 1–14 mmol/l variation of the flow concentration of  $\text{H}_2\text{S}$  the conversion rate of tetrahydrofuran increases and the order with respect to  $\text{H}_2\text{S}$  is approximately unity. Thus, the total order is first order, in agreement with experiments at different contact times. The process has been found to be inhibited by water and thiolane. The weight activity of the proton-donor catalysts determined at 360 °C, a ratio  $\text{H}_2\text{S}:\text{THF} = 1:5$ , and the same conversion of tetrahydrofuran (Table 13), depends on the acid-base characteristics of the surface. Amorphous  $\text{SiO}_2$  and silicates whose surfaces contain a large number of weak proton-donor centers possess low weight activities in the reaction of tetrahydrofuran with  $\text{H}_2\text{S}$  ( $W = 1\text{--}2 \text{ mmol/g}\cdot\text{h}$ ). The activity of one proton center equals  $1\text{--}2 \mu\text{mol/h}$ . The slightly higher activity of  $\text{SiO}_2$  is due to the fact that it has a certain amount of admixed cations with acceptor properties. The weight activity of  $\text{H}_3\text{PO}_4/\text{SiO}_2$  with a higher proton acidity is of the same order of magnitude as that of  $\text{SiO}_2$ , but the activity of one proton center is an order of magnitude higher and amounts to  $20 \mu\text{mol/h}$ . The selectivity towards thiolane drops to 6% for  $\text{H}_3\text{PO}_4/\text{SiO}_2$  compared to  $\text{SiO}_2$  with 20%. These results testify to the participation of proton centers in both the thiolane formation and the decomposition processes. The activity of  $\text{SiW}/\text{SiO}_2$  with

**Table 13.** The activity of proton-donor catalysts in the reaction of tetrahydrofuran with H<sub>2</sub>S at T = 360 °C<sup>118,119</sup>

| Catalyst   | 20% Conversion                                    |  | 50% Conversion                                    |  | W <sub>50%</sub><br>with respect to proton centers<br>$\frac{\mu\text{mol}}{\text{g}}$ |
|--|---|--|---|--|--|
|  | W,<br>$\frac{\text{mmol}}{\text{g}\cdot\text{h}}$ | Selectivity,<br>towards thio-<br>lane, % | W,<br>$\frac{\text{mmol}}{\text{g}\cdot\text{h}}$ | Selectivity<br>towards<br>thiolane,<br>% |  |
| SiO <sub>2</sub>                                     | 2.5   | 21                                       | 2.1   | 22                                       | 2  |
| Silicalite   | 1.0   | 30                                       | 0.7   | 50                                       | 1  |
| 30% H <sub>3</sub> PO <sub>4</sub> /SiO <sub>2</sub> | 2.2   | 6  | 1.0   | 3  | 20   |
| 5% SiW/SiO <sub>2</sub>                              | 3.7   | 22                                       | 3.3   | 22                                       | 55   |
| HZSM<br>(Si/Al 100)                                  | 7.5   | 22                                       | 10.4  | 20                                       | 200  |
| HZSM<br>(Si/Al 45)                                   | 27  | 32                                       | 22  | 30                                       | 170  |
| HNaY   | 33  | 60                                       | 22  | 48                                       | 200  |
| AlSi   | 11  | 30                                       | 11  | 22                                       | 200  |

stronger proton-donor centers is higher than that of the above catalysts calculated per both weight ( $W = 3.5 \text{ mmol/g}\cdot\text{h}$ ) and number of proton centers ( $55 \mu\text{mol/h}$ ). The weight and specific activity of aluminosilicates (amorphous AlSi and crystal HNaY and HZSM) are higher than those of other proton-donor catalysts. But this cannot be ascribed only to the participation of proton centers since these catalysts have strong Lewis acid and basic centers as well (Table 2). The contribution of these centers to the activity of catalysts for the reaction of tetrahydrofuran with H<sub>2</sub>S can be considerable, since they promote H<sub>2</sub>S activation. At the same time aluminosilicates, like the catalysts containing only proton centers, are of low selectivity towards the formation of thiolane. Apparently, this is due to the participation of the available strong proton centers in the decomposition and polymerization of tetrahydrofuran.

Interaction of tetrahydrofuran with acid solutions leads to a donor-acceptor complex with the participation of the tetrahydrofuran oxygen atom.<sup>128,129</sup> This results in ring opening and the formation of a carbenium ion which can be in equilibrium with other species:



It is likely that a similar process takes place in the presence of solid acids, e.g., zeolites.<sup>130,131</sup>

Adsorption studies of H<sub>2</sub>S on proton-donor catalysts show that at 20–300 °C it is weakly adsorbed on the surface (cf. pp. 283, 284) without noticeable activation. Taking into account the above facts the reaction on proton-donor catalysts can be suggested to take place via tetrahydrofuran adsorption on proton centers and further interaction with gaseous or slightly activated H<sub>2</sub>S to produce a surface intermediate product of H<sub>2</sub>S addition to an oxonium compound. Decomposition of this product yields thiolane and



**Table 14.** The activity of catalysts with paired centers in the synthesis of thiolane (at 80% conversion of tetrahydrofuran;  $[C_4H_8O] = 17 \text{ mmol/l}$ ,  $[H_2S] = 83 \text{ mol/l}$ )<sup>118</sup>

| Catalyst  | S,<br>m <sup>2</sup> /g | W,<br>mmol/g·h |
|---|-------------------------|----------------|
| NaX   | 800                     | 51             |
| NaY   | 800                     | 7              |
| $\gamma\text{-Al}_2\text{O}_3$                                      | 200                     | 690            |
| $\eta\text{-Al}_2\text{O}_3$  | 300                     | 850            |
| 3% HF/Al <sub>2</sub> O <sub>3</sub>                                | 200                     | 680            |
| 1.5% Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> | 290                     | 570            |
| 15% MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>                | 265                     | 380            |
| 10% K <sub>2</sub> CO <sub>3</sub> /SiO <sub>2</sub>                | 140                     | 0.1            |
| 3.7% NaOH/Al <sub>2</sub> O <sub>3</sub>                            | 280                     | 13             |
| 6.4% K <sub>2</sub> CO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> | 280                     | 24             |
| 25% K <sub>2</sub> WO <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>  | 154                     | 5              |

which forms thiolane by interaction with SH fragments. The participation of acid-basic pairs of centers in the H<sub>2</sub>S activation is confirmed by the fact that addition to the system of pyridine or HCl suppresses the acid and basic centers, respectively, and drastically decreases the formation of thiolane.<sup>116</sup> The interaction of an oxonium compound with SH fragments takes place at a higher rate than the competing polymerization and decomposition of tetrahydrofuran. Therefore NaX is more selective towards thiolane than proton-donor catalysts. It is likely that the reaction mechanism on NaY is the same as that on NaX. The differences in the rates are associated with the higher basicity of NaX compared to that of NaY and with the presence of a large number of delocalized sodium cations on NaX acting as acid centers.

More effective than Na zeolites are catalysts containing strong Lewis acid centers

**Table 15.** Thiolane formation from tetrahydrofuran and H<sub>2</sub>S on  $\gamma\text{-Al}_2\text{O}_3$ <sup>118,119</sup>

| T, °C | Concentration,<br>mmol/l        |                  | Contact time,<br>s | Conversion,<br>% | v,<br>mmol/g·h |
|-------|---------------------------------|------------------|--------------------|------------------|----------------|
|       | C <sub>4</sub> H <sub>8</sub> O | H <sub>2</sub> S |                    |                  |                |
| 100   | 0.6                             | 3.6              | 3.3                | 9                | 0.12           |
| 150   | 0.8                             | 3.9              | 2.6                | 21               | 0.46           |
| 150   | 0.7                             | 0.4              | 3.5                | 16               | 0.23           |
| 200   | 0.7                             | 3.5              | 1.3                | 66               | 2.6            |
| 200   | 0.7                             | 0.8              | 2.2                | 44               | 1.0            |
| 300   | 0.8                             | 2.7              | 0.010              | 76               | 500            |
| 300   | 0.6                             | 5.3              | 0.014              | 95               | 360            |
| 320   | 7.4                             | 37.3             | 0.04               | 42               | 650            |
| 360   | 0.6                             | 0.7              | 0.01               | 22               | 108            |
| 360   | 0.5                             | 1.5              | 0.004              | 31               | 450            |
| 360   | 0.5                             | 3.8              | 0.0025             | 29               | 620            |
| 360   | 0.5                             | 10.3             | 0.001              | 18               | 900            |
| 360   | 3.4                             | 9.4              | 0.003              | 14               | 1400           |
| 360   | 6.8                             | 9.8              | 0.01               | 22               | 1600           |
| 360   | 7.5                             | 37.3             | 0.04               | 65               | 990            |
| 360   | 7.2                             | 37.4             | 0.11               | 92               | 514            |
| 360   | 7.2                             | 37.4             | 0.16               | 100              | 500            |
| 400   | 7.3                             | 37.3             | 0.04               | 86               | 1200           |



paired with basic ones, e.g., coordinatively unsaturated  $\text{Al}^{3+}$  ions in alumina. The reaction of tetrahydrofuran with  $\text{H}_2\text{S}$  starts at about  $100^\circ\text{C}$ . The yield of thiolane grows with increasing temperature and contact time and depends on the concentration of reactants.<sup>118,119</sup> The weight activity of  $\text{Al}_2\text{O}_3$  is an order of magnitude higher than that of  $\text{NaX}$  (Tables 14 and 15).

$\text{H}_2\text{S}$  is dissociatively chemisorbed on  $\text{Al}_2\text{O}_3$  to form surface SH fragments bound to Al. Alumina has weak proton centers as determined by ammonia adsorption. Due to the dissociation of  $\text{H}_2\text{S}$  stronger proton-donor centers are formed. They can participate in the activation of tetrahydrofuran to produce an oxonium compound which reacts with SH fragments to form thiolane. But this reaction mechanism does not account for the very high reaction rate on  $\text{Al}_2\text{O}_3$  compared to that on  $\text{NaX}$  for which a similar mechanism has been suggested. Apparently, the reaction on  $\text{Al}_2\text{O}_3$  involves the participation of basic and strong Lewis acid centers.

In solutions tetrahydrofuran coordinates to Al, Ga, Sn, B, Ti, and Fe halides<sup>128,132</sup> to form a donor-acceptor complex  $\text{C}_4\text{H}_8\text{O} \rightarrow \text{Al} \leftarrow$ . A similar process is also possible on Lewis acid centers of solid catalysts. For example, the adsorption of tetrahydrofuran on  $\text{Al}_2\text{O}_3$  is accompanied by a decrease in the concentration of Lewis acid centers as determined by the spectral test molecule method.<sup>118,119</sup>

Oxonium compounds can decompose at the C-O bond and produce decomposition products. Under the effect of strong Lewis acid centers tetrahydrofuran can be polymerized.<sup>120,121,133</sup> But, as in the above processes on  $\text{Al}_2\text{O}_3$  when they do take place, their importance is small due to the high rate of the interaction between reactive SH fragments and surface oxonium compounds. This leads to the high selectivity towards thiolane (Figure 9).

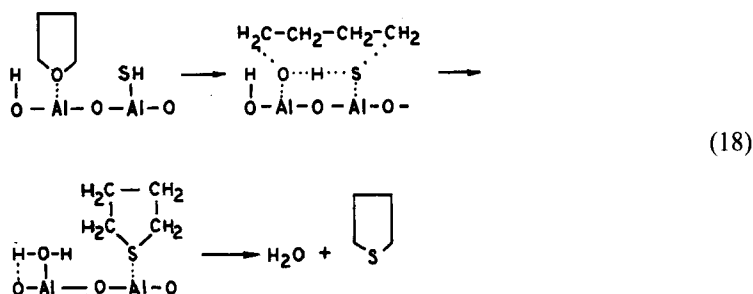
The formation rate of thiolane on alumina depends on the partial pressures of the reactants and is inhibited by the products.

The reaction rate follows the equation:

$$v = \frac{K \cdot P \cdot P_{\text{H}_2\text{S}}}{(1 + b_1 P_{\text{T}} + b_2 P_{\text{H}_2\text{O}})^2}$$

where  $P$ ,  $P_{\text{H}_2\text{S}}$ ,  $P_{\text{T}}$ ,  $P_{\text{H}_2\text{O}}$  are the partial pressures of tetrahydrofuran,  $\text{H}_2\text{S}$ , thiolane and water, respectively.

The kinetic data agree with a fast adsorption of the reactants (to form a surface oxonium compound with an aluminum cation and SH and OH groups on acid-basic paired centers) and a slow interaction between these surface species to form thiolane and water:



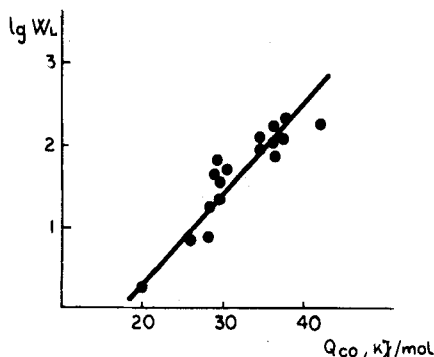
This scheme is similar to Scheme 17, but the oxonium compound is formed with the participation of Lewis acid centers. Besides, this scheme provides a more detailed description of the participation of SH fragments in the process. This participation is confirmed by NMR studies of adsorption at temperatures below 200 °C. Joint adsorption of tetrahydrofuran and H<sub>2</sub>S on Al<sub>2</sub>O<sub>3</sub> is confirmed by the disappearance of a signal assigned to SH fragments ( $\delta = -1.7$  ppm) and tetrahydrofuran associatively bonded to the surface ( $\delta = 3.63$  and 1.79 ppm).

Modification of alumina with acid promoters (chromium, molybdenum, boron oxides, or mineral acids) results in increasing strength of the Lewis acid centers, but their concentration slightly decreases. There appear low concentrations of strong proton-donor centers and the basicity of the catalysts diminishes (Table 2). The activity of these catalysts in thiolane formation is only slightly lower than that of alumina (Table 14). This testifies to the more important role of the strength of Lewis acid centers in acid-base pairs for the activity of catalysts for the formation of thiolane from tetrahydrofuran and H<sub>2</sub>S.

A K<sub>2</sub>CO<sub>3</sub>/SiO<sub>2</sub> catalyst does not contain acid centers, but has only strongly basic centers on its surface (Table 2). Its activity is lower by a factor of 30 than that of the support, i.e. silica. Modification of alumina with potassium or sodium hydroxide, carbonate, or tungstate<sup>16</sup> leads to the formation of strongly basic surface centers (PA<sup>b</sup> = 930–970 kJ/mol). The selectivity towards thiolane on these catalysts is 100%, but the activity of the catalysts is lower than that of Al<sub>2</sub>O<sub>3</sub>. With varying concentration of sodium hydroxide on Al<sub>2</sub>O<sub>3</sub> (Table 16) the total content of strongly basic centers changes slightly. No straightforward relationship with the activity has, however, been found. With low concentrations of alkalis added to alumina the proton centers are primarily suppressed, whereas the Lewis acid centers remain unaffected. The weight activity of the catalysts varies slightly with increasing NaOH concentration up to 0.1 wt.%. This suggests that the proton-donor centers of alumina catalysts do not contribute to the synthesis of thiolanes. As the NaOH concentration in Al<sub>2</sub>O<sub>3</sub> rises, the

**Table 16.** The influence of NaOH additives to Al<sub>2</sub>O<sub>3</sub> on its activity in the reaction of tetrahydrofuran with H<sub>2</sub>S at T = 360 °C, 50% conversion of tetrahydrofuran, and a ratio H<sub>2</sub>S:THF = 1:5<sup>119</sup>

| NaOH additive<br>to $\gamma$ -Al <sub>2</sub> O <sub>3</sub><br>Wt.% | $\mu\text{mol/g}$ | S,<br>m <sup>2</sup> /g | Concentration of<br>centers, $\mu\text{mol/g}$<br>Lewis acid<br>Q <sub>CO</sub> = 34–20 kJ/mol | Basic<br>PA <sup>b</sup> > 900 kJ/mol | Catalyst<br>activity,<br>mmol/g·h |
|--|-------------------|-------------------------|--|---------------------------------------|-----------------------------------|
| 0  | 0                 | 200                     | 550  | 814                                   | 530                               |
| 0.01   | 2.5               | 200                     | 500  | 816                                   | 550                               |
| 0.02   | 5.0               | 230                     | —  | —                                     | 530                               |
| 0.05   | 12.5              | 220                     | 880  | 580                                   | 474                               |
| 0.1  | 25                | 210                     | 830  | 770                                   | 500                               |
| 0.25   | 62.5              | 200                     | —  | —                                     | 386                               |
| 0.30   | 75                | 210                     | 810  | 800                                   | 343                               |
| 0.5  | 125               | 230                     | 970  | —                                     | 224                               |
| 1.0  | 250               | —                       | 750  | 580                                   | 128                               |
| 3.0  | 750               | 230                     | 460  | 780                                   | 32                                |
| 5.0  | 1250              | 220                     | 280  | 740                                   | 17                                |
| 10.0   | 2500              | 200                     | —  | 100                                   | 10                                |



**Figure 10.** The logarithmic dependence of the catalyst activity in thiolane formation from tetrahydrofuran and hydrogen sulfide ( $v \cdot 10^2$  mmol/g·h) per one Lewis acid center on this center strength,  $T = 360^\circ\text{C}$ ,  $\text{H}_2\text{S}:\text{C}_4\text{H}_8\text{O} = 5$ .<sup>119</sup>

strength of the Lewis acid centers decreases and the weight activity of the catalysts drops. The activity of one Lewis acid center diminishes as its strength drops (Tables 14 and 16, and Figure 10).

These results indicate that thiolane formation requires the presence of strong Lewis acid centers on the surface of alumina catalysts. These centers take part in the formation of an oxonium complex of tetrahydrofuran and paired with basic centers they promote  $\text{H}_2\text{S}$  activation. Compared to proton-donor catalysts, samples having strong Lewis acid centers, especially paired with basic ones, are more effective, since on their surface tetrahydrofuran is considerably activated and reactive SH fragments are formed readily from molecular  $\text{H}_2\text{S}$ . These fragments interact with oxonium compounds to form thiolane.

In the course of the reaction the initial activity of the alumina catalysts decreases, although more slowly than that of proton-donor samples. Their surfaces accumulate carbon deposits. Apparently, their deactivation takes place under the effect of the products of tetrahydrofuran deoxygenation. According to,<sup>134</sup> on  $\text{Al}_2\text{O}_3$  and Al-Co-Mo catalysts in nitrogen at  $400^\circ\text{C}$  tetrahydrofuran decomposes to yield mainly propylene and butadiene and also butenes. The butadiene has been suggested to be formed from tetrahydrofuran chemisorbed via its oxygen atom on  $\text{Al}^{3+}$  cations with subsequent dissociation of both C-O-C bonds. When the first C-O bond is dissociated, the structure formed can further decompose to produce butene or, which is more probable, propylene and formaldehyde-like O- $\text{CH}_2$  structures. The resinous deposits are formed by butadiene polymerization or by condensation of surface O- $\text{CH}_2$  structures and unsaturated hydrocarbon moieties. NMR studies of tetrahydrofuran interaction with  $\text{Al}_2\text{O}_3$  show that at temperatures below  $200^\circ\text{C}$  it is associatively adsorbed by the catalyst. At higher temperatures the adsorption is accompanied by tetrahydrofuran decomposition to yield butenes ( $\delta = 0.83$  and  $1.0$  ppm) and  $\text{CH}_4$  ( $\delta = 0.96$  ppm). At  $400^\circ\text{C}$  the reaction produces aromatic and olefinic compounds ( $\delta = 7.3$  and  $4.4$  ppm). In the presence of  $\text{Al}_2\text{O}_3$  at  $T = 100$ – $200^\circ\text{C}$  in helium tetrahydrofuran decomposes at high rates and yields mainly  $\text{C}_3$  hydrocarbons. The decomposition rate rises with increasing temperature, up to  $300^\circ\text{C}$ . Besides  $\text{C}_3$ , the products contain the same amount of  $\text{C}_4$

hydrocarbons and also a small amount of  $C_1$ . A carbon deficit (30–40%) in the material balance and a decrease in the catalyst activity with time (e.g. 20% decrease after 30 min) are observed. Evolution of gaseous hydrocarbons and catalyst deactivation are also observed in experiments with low concentrations of  $H_2S$  and a ratio  $H_2S:C_4H_8O \leq 1$ .

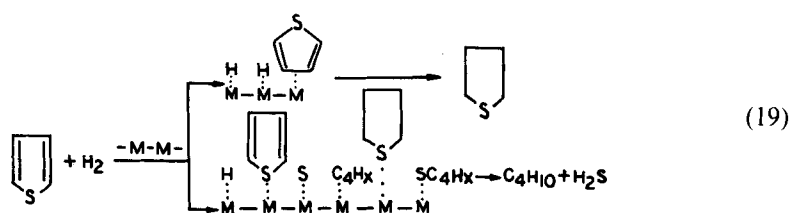
Thus, the selective formation of thiolane on alumina catalysts and the stable operation of the contacts require moderate reaction temperatures and excess  $H_2S$  relative to tetrahydrofuran.

*II.2.2. Catalytic hydrogenation of thiophenes* Thiolanes can be obtained from more readily available thiophene derivatives. For this purpose noncatalytic reduction of thiophenes with the systems: zinc-proton acid, triethylsilane-trifluoroacetic acid, etc. has been suggested.<sup>135,136</sup> These methods require a large excess of reactants, the reduction rate is low, and the reactivities of the thiophenes are greatly dependent on their structures. A more efficient method is the reduction of thiophenes with molecular hydrogen, which requires catalysis.

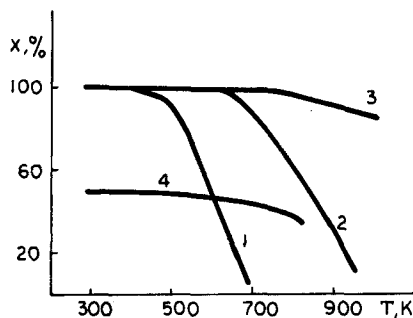
Thiophenes can coordinate with catalysts both with involvement of their  $\pi$ -electrons and of the sulfur atom. Molecules activated via  $\pi$ -bonding can be saturated by hydrogen activated by the same catalyst.

Hydrogenation catalysts are substances capable of forming complexes with unsaturated compounds and with hydrogen: group VIII metals, their complexes, and transition-metal sulfides.<sup>137</sup>

The activity of the platinum group metals in hydrogenation is largely associated with their "dative" ability, i.e. the metal-to-reactant transfer of electron density. The metals activate unsaturated compounds by forming  $\pi$ -alkene complexes. Hydrogen activation takes place by transfer of electron density from an occupied metal atomic orbital to a vacant antibonding molecular orbital of hydrogen. Certain thiophenes and thiolanes coordinate to metals with formation of  $M-S$  bonds. This leads to a decrease in the number of active centers and to a change in their electronic properties and hence makes the reaction difficult. In the case of vigorous interaction with a catalyst, thiophenes and their saturated derivatives decompose with elimination of  $H_2S$  or sulfur and of alkenes which deactivate the catalyst:



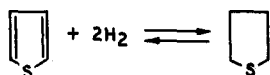
Hydrogenation of unsaturated organic compounds can also take place in the presence of transition-metal sulfides.<sup>8</sup> Hydrogenation mechanisms on metal sulfides have been studied in less detail than those on metals. XPS and quantum chemical data<sup>138</sup> suggest that metal sulfides possess acceptor centers formed by displacement of electron density from the metal to sulfur atoms of the catalyst. It is this displacement which is responsible



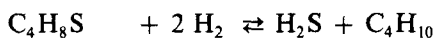
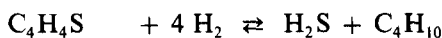
**Figure 11.** The temperature dependence of the equilibrium depth of thiophene hydrogenation to thiolane (1), thiophene and thiolane hydrogenolysis (2, 3), and thiophene hydrogenation and hydrogenolysis (4).<sup>139</sup>

for an activation different from that on metals, i.e. the complex formation takes place due to transfer of electron density from hydrogen and alkenes to a cation. The donation of electrons to a hydrogen orbital which occurs on platinum group metals weakens the bond between the hydrogen atoms more intensively than a donor-acceptor interaction where hydrogen electrons are transferred to vacant metal orbitals in sulfides. This can be the reason for the more difficult course of hydrogenation on sulfides than on metals. Besides, the distance between the metal atoms in sulfides is greater than that in metals. For a certain type of molecules (when structural correspondence is important) this implies a decrease in the concentration of active centers. All this makes the reaction more difficult and it must be carried out under more severe conditions, in particular at elevated temperatures. There are also some other difficulties associated with the mechanism of the activation of the substrates. For example, the donor-acceptor interaction of thiophenes with metal sulfides involves the participation of both carbon atoms of a C=C group and the sulfur atom of a thiophene. This decreases the number of active centers with respect to hydrogenation and increases the probability of thiophene ring cleavage.

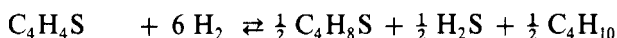
Calculations show that thiophene hydrogenation can be complicated by hydrogenolysis since both of these reactions are of high thermodynamic probability. With a stoichiometric hydrogen-to-thiophene ratio the equilibrium yield of thiolane in the reaction



increases with decreasing temperature (Figure 11). With 10–100 times excess hydrogen relative to thiophene and at increased pressures the equilibrium yield of thiolane is 100% at  $T < 830\text{ K}$ . But under these conditions the hydrogenolysis of thiophene and of thiolane is even more probable:



Hence at certain temperatures, even with a 100-fold excess of hydrogen, the equilibrium yield of thiolane cannot exceed 50% since the following reaction



takes place. This does not mean, however, that a high yield of the product of thiophene saturation (thiolane) cannot be obtained. The mechanisms of these two processes are different. It is most probable that the hydrogenolysis taking place at increased temperatures and occurs in several steps. One of these steps requires the formation of a surface complex involving the participation of the thiophene sulfur atom with further dissociation of the C-S bond in the chemisorbed molecule, whereas for thiophene saturation to thiolanes a dative bond must be realized due to the formation of a surface  $\pi$ -alkene complex. Thus, hydrogenation and hydrogenolysis involve the participation of different active centers of the catalysts. Hence it is possible by proper choice of the catalyst and the reaction conditions to direct the process towards the saturation of a thiophene to a thiolane.

The response of the hydrogenation to the reaction conditions has been established for thiophenes and their close homologs as examples. Some attempts have been made to realize this reaction on various catalysts in both liquid- and gas-phase processes.

*II.2.2.1. Gas-phase hydrogenation* Gas-phase hydrogenation has been studied in detail in connection with the elaboration of the complete hydropurification processes. In several cases the hydrogenolysis of thiophenes on catalysts containing molybdenum, cobalt, nickel, tungsten, and chromium sulfides at 200–350 °C produced thiolanes<sup>139–143</sup> with 1–3 and 10–34% yield at atmospheric and increased pressure, respectively.

In the presence of CaA, CaX and CaY zeolites modified with nickel or cobalt, thiophene reduction takes place. On nickel-containing CaY zeolites at atmospheric pressure,  $T = 250\text{--}300\text{ }^\circ\text{C}$  and contact times of 1.5–3 s, the thiolane yield is 90–98%, but the catalysts are deactivated. For the duration of the steady-state process (0.5–1.0 h) 0.35 g thiolane per 1 g catalyst is obtained.<sup>144</sup> On NiHNaY zeolites prepared via ion exchange with nickel ammoniate and with highly dispersed nickel in their intracrystal cavities, at  $T = 250\text{--}325\text{ }^\circ\text{C}$  and 0.1–2.5 MPa hydrogen pressure the yield of thiolane from thiophene is 70%. In the course of the experiment the catalyst activity decreases. The main reason for the catalyst deactivation is the formation of coke deposits which diminishes the catalyst surface accessible to the reactants. The catalysts can be partly regenerated by treatment with air.<sup>145,146</sup> More stable in gas-phase processes is palladium sulfide supported by alumina. At temperatures  $T = 190\text{--}220\text{ }^\circ\text{C}$  and 0.1–5.0 MPa pressure the yield of thiolanes can be as high as 60 mol.% with a selectivity of 80–90%. The catalyst activity does not decrease during 90 h operation and no less than 20 g thiolane is obtained per 1 g catalyst.<sup>147,148</sup>

*II.2.2.2. Liquid-phase hydrogenation* Liquid-phase hydrogenation of thiophenes takes place under the effect of various catalysts.

Metallic rhodium (1.2% Rh/Al<sub>2</sub>O<sub>3</sub>) at 20 °C and atmospheric pressure is of low activity and stability. For example, with excess catalysts with respect to thiophene the yield of thiolane equals 5–6 mol.%. The hydrogenation ceases after the formation of 0.035 g thiolane per 1 g catalyst.<sup>149</sup> Rhodium complexes with anthranilic or *N*-phenyl-anthranilic acid dissolved in *N,N*-dimethylformamide at atmospheric pressure are of low

**Table 17.** Hydrogenation of sulfur compounds on 5% Pd/C at 20 °C and 0.1 MPa in methanol solution

| Compound                                      | Reaction rate, $v \cdot 10^2$ , mol/g Pd·h | Product yield before catalyst deactivation, mol/g Pd·10 <sup>2</sup> | 100% yield of product at catalyst content (% of substrate weight) |
|---|--|--|---|
| C <sub>4</sub> H <sub>4</sub> S               | 3  | 1  | 2500  |
| CH <sub>3</sub> SCH=CH <sub>2</sub>           | 7  | 2  | 200   |
| CH <sub>2</sub> =CH-CH <sub>2</sub> SH        | 30   | 5  | 150   |
| C <sub>4</sub> H <sub>6</sub> SO <sub>2</sub> | 120  | 1500   | 0.1   |

activity in homogeneous hydrogenation.<sup>150</sup> More active are palladium catalysts. Hydrogenation of thiophenes and their derivatives has been carried out<sup>151</sup> at 20 °C and 0.2–0.4 MPa for 0.5–2.0 h in a solution of methanol modified with 1 wt. % H<sub>2</sub>SO<sub>4</sub>, in the presence of 5% Pd supported on catalyst a 100% yield of thiolane is obtained after 0.5 h with a formation rate of 1.6 g/h per 1 g Pd. With a small amount of catalyst the reaction rate is low and the process remains incomplete due to catalyst deactivation. The reaction rate is much lower (by a factor of 2–40) compared to that for the liquid-phase hydrogenation of other unsaturated sulfur compounds (Table 17). Apparently, aromatic C=C bonds are more difficultly activated than olefinic ones.<sup>152,153</sup>

The formation rate of thiolane is slightly dependent on the quantity of palladium and on its dispersity on various carriers (AlSi, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and carbon)(cf. Table 18). With the pressure rising from 0.1 to 5 MPa a five-fold increase in the reaction rate at 20 °C is observed. The hydrogenation partly takes place via the hydrogen adsorbed by the palladium<sup>152</sup> (Table 19).

Thiophene reduction in polar solvents (alcohols, *N,N*-dimethylformamide) is easier than in hydrocarbons.<sup>154</sup> When the hydrogenation temperature rises from 20 to 80 °C at 0.5 MPa, the formation rate of thiolanes increases slightly. At higher temperatures the formation rate increases considerably, but under these conditions palladium sulfuriza-

**Table 18.** Hydrogenation of thiophene in the presence of supported metallic palladium in alcohols, hydrocarbons, and thiolane 1,1-dioxide<sup>153,155</sup>

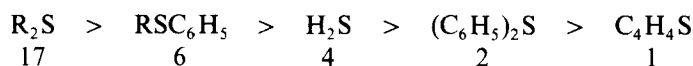
| Catalyst  | T, °C | P, MPa | W, mol thiolane                                |           | Thiolane yield,             |      |
|---|-------|--------|--|-----------|-----------------------------|------|
|   |       |        | $\frac{1 \cdot h}{\text{per g accessible Pd}}$ | g 5% Pd/C | mol per g-at. accessible Pd |      |
| 1–10% Pd on   | 20    | 0.1    | 0.2  | 0.006     | 0.4                         | 0.01 |
| Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , | 60    | 0.1    | 0.4  | 0.012     | 0.8                         | 0.02 |
| coal  | 20    | 5.0    | 0.9  | 0.03      | 2.0                         | 0.05 |
|   | 80    | 5.0    | 1.1  | 0.04      | 4.3                         | 0.1  |

**Table 19.** Hydrogenation of thiophene on Pd/carbon catalyst (20 °C, 5 MPa, solvent: thiolane 1,1-dioxide with 1% H<sub>2</sub>SO<sub>4</sub>)<sup>152</sup>

| Amount of thiophenes taken for hydrogenation, g | Reaction medium | Hydrogenation time, min | Yield of thiolane, mol. % |
|---|-----------------|-------------------------|---------------------------|
| 0.1   | Hydrogen        | 10                      | 29                        |
|   | Hydrogen        | 15                      | 36                        |
|   | Hydrogen        | 30                      | 40                        |
|   | Hydrogen        | 45                      | 45                        |
| 0.1   | Hydrogen        | 30                      | 1                         |
| 0.1 (additional)                                | Nitrogen        | 10                      | 9                         |
|   | Nitrogen        | 15                      | 10                        |
|   | Nitrogen        | 30                      | 11                        |
|   | Nitrogen        | 45                      | 10                        |

tion takes place depending on the reaction medium.<sup>155</sup> Metal palladium catalysts are extremely unstable at  $T = 20\text{--}80\text{ }^\circ\text{C}$ .<sup>153</sup> Apparently, their deactivation mainly takes place by interaction of the palladium with thiolane to form a donor-acceptor bond  $\text{Pd} \leftarrow \text{S} \leftarrow$ . This bond is stronger than that of palladium with thiophenes coordinating over the  $\pi$ -electron system. The catalyst toxicity of sulfur compounds rises with increasing donor ability of their sulfur atoms. For example, saturated thiols are weaker electron donors than thiolanes and their bonds with palladium are weaker. Under the reaction conditions thiols are partly desorbed from the surface and hence the stability of the catalyst is an order of magnitude higher than that in the hydrogenation of thiophenes to thiolanes.

The relative catalyst toxicities of sulfur compounds were found to lie in the following sequence:



In the presence of organic sulfides the stability of palladium hydrogenation catalysts increases with increasing donor ability of the sulfur atoms.<sup>152</sup>

A further reason for catalyst deactivation, besides its blocking by thiolane, can be the formation of surface PdSR and PdS<sub>x</sub> compounds. As a consequence the stability of a palladium catalyst in thiophene hydrogenation is three orders of magnitude lower than in the hydrogenation of alkenes which do not contain bivalent sulfur (Table 17).

Irrespective of the substrate type, the palladium content on it, and the hydrogenation conditions (solvent, acidity, temperature, pressure, and thiophene content in the initial solution) complete deactivation of palladium catalysts in thiophene hydrogenation takes place after the formation of no more than 4.5 moles of thiolane per 1 g-atom of accessible metal. This corresponds to approximately 0.1 g thiolane yield from 1 g 5% Pd substrate catalyst (Table 18). The deactivation of metallic palladium cannot be prevented.<sup>153</sup>

Thiophene reduction is catalyzed by metal complexes. It takes place under the effect of dicobaltocarbonyl at  $T = 180\text{--}190\text{ }^\circ\text{C}$  and  $P = 20\text{--}28\text{ MPa}$ . Such catalysts are deac-



tivated by sulfurization.<sup>156</sup> Metal complexes of palladium with alizarin C (0.5 wt.%) supported on  $\text{Al}_2\text{O}_3$  enhance thiophene hydrogenation (200 °C, 16 MPa, 4–7 h contact time, 0.04–0.2 mol.% with respect to substrate). The yield of thiolane rises depending on the type of solution used. The maximum yield of 10–11.4 mol.% was obtained in 2-propanol and methylcyclohexane. The effect of the solvents is attributed to their ability to solvate the reactants on the catalyst surface.<sup>157</sup>

Palladium complexes supported on  $\text{SiO}_2$  catalyze the hydrogenation of thiophene to thiolane at 20 °C and 0.1–5.0 MPa. Their activity is of the same order of magnitude as that of metallic palladium. With the temperature increasing to 80 °C at 5 MPa the hydrogenation rate grows by a factor of 16, but at the same time the structure of the complexes changes. With respect to their stability these complexes are close to metallic palladium (Table 20).<sup>153,155</sup>

The reason for the deactivation of  $\text{SiO}_2$ -supported palladium complexes was established by hydrogenation of a compound which is not toxic for these catalysts. 3-Thiolene 1,1-dioxide was added to solutions of thiophene or thiolane.<sup>158,159</sup> In the presence of the latter the initial activity of these complexes decreases, and an especially strong poison is thiolane. The formation constant of the adsorptive thiophene-catalyst complexes is a factor of 3 smaller than that for thiolane complexes. As follows from desorption data the deactivation by thiophenes is partly reversible, whereas the toxic effect of thiolanes is irreversible. In *N,N*-dimethylformamide which is a good complex formation agent in competition with sulfur-containing poisons the stability of the complexes towards the poisoning effect is higher than in isopropanol (at a poison to catalyst ratio of 100:1). The stability of mononuclear complexes of Pd(II) depends on the donor ability of internal ligands and is represented by the instability constants of

**Table 20.** Hydrogenation of thiophene in the presence of palladium complexes<sup>153,155</sup>

| Catalyst  | T,<br>°C | $P_{\text{H}_2}$ ,<br>MPa | v,<br>mmol<br>g-at. Pd·min | Stability,<br>mol<br>g-at. Pd |
|---|----------|---------------------------|----------------------------|-------------------------------|
| Supported Pd  | 20       | 0.1                       | 6                          | 0.4                           |
| ( $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ , C)   | 20       | 5.0                       | 30                         | 2.0                           |
|   | 80       | 5.0                       | 35                         | 4.3                           |
| Mononuclear complexes of Pd(II):  | 20       | 0.1                       | 2–4                        | 0.4–1.4                       |
| $\text{Si}-(\text{CH}_2)_3\text{L}'\text{PdL}''$  | 20       | 5.0                       | 5–16                       | 1.4–2.0                       |
| ( $\text{L}'-\text{C}_6\text{H}_4\text{C} \begin{array}{l} \diagup \text{NH}_2 \\ \diagdown \text{=NOH} \end{array}$ )  | 80       | 5.0                       | 30–80                      | 2–8                           |
| $\text{NHCS}_2\text{Na}$ , $\text{C}_8\text{H}_8\text{NS}$ ,<br>$\text{L}' = \text{Cl}$ , $\text{OAc}$ , $\text{OH}$ )  | 20       | 0.1                       | 11                         | 2.0                           |
| of Pd(0):<br>$\text{Si}-\text{CH}_2\text{CH}_2\text{PPh}_2\text{Pd}(\text{PhCH}=\text{CH})_2\text{CO}$  | 20       | 0.1                       | 4–40                       | 0.4–3.4                       |
| Polynuclear complexes of Pd:  |          |                           |                            |                               |
| $\text{Si} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2\text{PPh}_2 \\ \diagdown \text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{PPh}_2 \end{array} \text{Pd}_n\text{L}$ | 20       | 0.1                       | 24                         | 2.0                           |
| ( $n = 2-6$ , $\text{L} = \text{OAc}$ , $\text{Cl}$ )   | 80       | 5.0                       | 63                         | 4.4                           |
| $\text{Si}-\text{CH}_2\text{CH}_2\text{PPh}_2\text{Pd}_n$ ( $n = 2, 3$ )  | 20       | 0.1–5.0                   | 0                          | 370                           |
| $\text{PdS}/\text{Al}_2\text{O}_3$  | 200      | 5.0                       | 170                        |                               |

these complexes. With their decrease the strength of the Si-L-Pd bond increases and the ability of the palladium to coordinate with a poison to form  $\text{Si-L-Pd} \leftarrow \text{S} \leftarrow$  diminishes. The stability of polynuclear complexes depends on both the strength of the Pd bond with internal ligands and on steric factors. The contribution of the latter increases with the nuclearity. Due to the small size of the cluster framework, not all the palladium atoms are accessible for the formation of bonds to the poison, but they are all accessible for hydrogen activation.

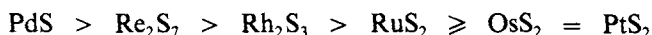
According to XPS data mononuclear complexes of Pd(II) treated with thiolanes undergo changes. In the spectral region Pd-3d one can observe a decrease in the bond energy from 337.2 to 336.7 eV at  $B = 3.4\text{--}3.5$  eV, which testifies to a decreased valency of palladium. The intensity changes only slightly (0.23–0.21). In the region S-2p and S-2s the spectrum exhibits sulfur lines. UV spectra of samples treated with a poison exhibit a shoulder at  $34\,000\text{--}24\,000\text{ cm}^{-1}$ , typical for a Pd(II) bond to sulfur. XPS spectra of Pd(0) complexes, untreated and treated with thiolanes, respectively, exhibit constant bond energies with line half-widths of 336.1 and 4.4–4.1 eV respectively. The intensities of the lines Pd-3d/Si-2p decrease from 0.36 down to 0.26, which can be ascribed to screening of the palladium signal by adsorbed poison molecules. The UV spectra also show preservation of the complex structure after treatment with thiolane (bands at  $28\,000$ ,  $22\,000$  and  $16\,000\text{ cm}^{-1}$ ). Treatment of Pd(0) complexes with high quantities of poisoning substances at elevated temperatures destructs the initial structure according to XPS data which show a decrease in the bond energy, the half-widths of the lines, and the signal intensities. This is also confirmed by the disappearance from the UV spectra of bands typical for the initial complexes. Apparently, the complex destruction is accompanied by the formation of the  $\text{Pd} \leftarrow \text{S} \leftarrow$  bond.

Thus SiO<sub>2</sub>-supported palladium complexes are deactivated due to the fact that sulfur poisons entering into the coordination sphere of palladium remove external ligands and form palladium-sulfur bonds. Under certain conditions the structure of these complexes is completely destroyed.

Transition-metal sulfides are active in the reduction of thiophenes at temperatures above 100 °C and high hydrogen pressures.<sup>160–162</sup> For example, in the hydrogenation of alkyl- and acetylthiophenes on CoS<sub>x</sub> catalysts at 200–225 °C, 10 MPa, and 2–13 h reaction time the yield of substituted thiolanes is 15–95%. Molybdenum sulfide at 230–300 °C and 14–17 MPa is hardly active in thiophene hydrogenation. More active are sulfides of the platinum and rhenium group metals (both in bulk and supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, AlSi, and carbon): at 150–250 °C and 3–25 MPa with 3–40 wt.% catalyst with respect to thiophenes in alcohol or hydrocarbon solution the yield of thiolanes is 60 mol.% with 70–90% selectivity.

The best results were obtained on palladium sulfides. For example, in the hydrogenation of thiophene catalyzed by 2.5% PdS/Al<sub>2</sub>O<sub>3</sub> (200 °C, 25 MPa, 3 h), the yield of thiolane is 60% with respect to starting thiophene and about 100% with respect to consumed thiophene. The catalyst productivity is 18 g/h thiolane per 1 g palladium.<sup>160</sup>

With regard to their relative specific catalytic activities these metal sulfides were found<sup>160</sup> to form the sequence:

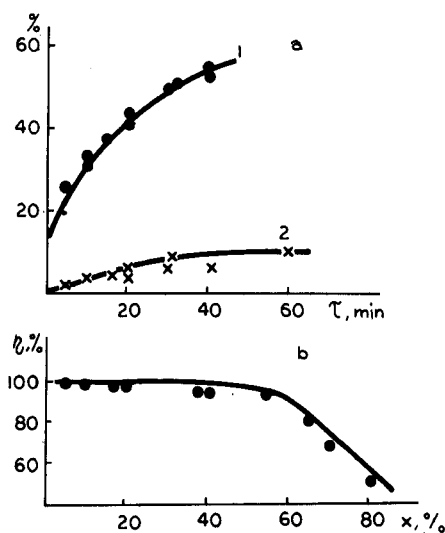


Hydrogenation of thiophene and 2-methylthiophene in the presence of modified sulfide-

palladium catalysts<sup>147,148,154</sup> takes place at 260 °C and 5 MPa in dodecane solution (0.1–5 mol/l) with up to 60% yield after 0.5 h and a selectivity towards thiolanes as high as 70%. With up to 50% conversion of thiophenes the selectivity towards thiolanes is 90–97%. These catalysts are stable for extended hydrogenation periods: no less than 20 g thiolane can be obtained per 1 g catalyst and the catalyst productivity is as high as 12 g/g·h.

Supported PdS catalysts are approximately 1000 times more stable than the corresponding metallic palladium samples, though their initial activities under the above conditions do not differ.<sup>160</sup>

After thiophene hydrogenation the sulfur content in Pd/Al<sub>2</sub>O<sub>3</sub> catalysts is the same as in PdS/Al<sub>2</sub>O<sub>3</sub> samples, apparently due to metal sulfurization. Thermodynamic calculations predict easy sulfurization of palladium.<sup>163</sup> To preserve the PdS phase at 327 °C and 0.1 MPa, about 3% H<sub>2</sub>S must be present in the equilibrium state. Experimental data indicate<sup>160</sup> that metallic palladium supported on Al<sub>2</sub>O<sub>3</sub> completely transforms to palladium sulfide already after 0.5 h treatment with H<sub>2</sub>S at 200 °C. At the same time thermodynamic calculations for the PdS + H<sub>2</sub> system show that at moderate temperatures (below 500 °C) palladium sulfides can be partially reduced to metallic palladium.<sup>164</sup> A considerable amount of metallic palladium must be formed with increasing partial pressure of hydrogen in the system. Besides metallic Pd, the equilibrium system must also contain Pd<sub>2</sub>S whose content rises with temperature and the ratio H<sub>2</sub>:PdS. Thus, in the course of the hydrogenation of thiophenes (100–300 °C) on palladium sulfide catalysts the latter can gradually be reduced to form either metal- or sulfur-deficient phases. These suggestions have been confirmed by XPS and thermostimulated exoelectron emission studies.<sup>138</sup> The reduction of palladium sulfide by hydrogen is slower than the sulfurization of metallic palladium. At 200 °C the extent of reduction after 1 and



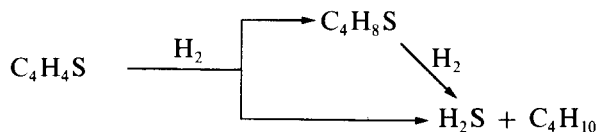
**Figure 12.** The hydrogenation of 2-methylthiophene over PdS/Al<sub>2</sub>O<sub>3</sub> at  $t = 260$  °C,  $P = 5$  MPa in dodecane. (a) The influence of the contact time on the yields of 2-methylthiolane (1) and pentane (2); (b) The dependence of the selectivity towards 2-methylthiolane on 2-methylthiophene conversion.<sup>154</sup>

10 h was 2 and 85%, respectively. Complete reduction requires 50 h.<sup>160</sup> In the course of liquid-phase hydrogenation of thiophene in the presence of rhenium sulfide the sulfur concentration in the bulk and in the near-surface layer of the catalyst decreases as evident from chemical analysis and XPS data.<sup>157</sup>

The reduction of metal sulfides to metals under catalytic conditions is difficult, since as a consequence of the dissociative chemisorption of the sulfur compounds the catalyst is sulfurized. In addition, the catalyst is stabilized by complex formation involving a sulfur atom of the undissociated compound. Hence it is most likely that the active component of the catalysts for thiophene hydrogenation at elevated temperatures is the metal sulfide.

Kinetic studies<sup>148,160</sup> show that the curves of the thiolane yield in thiophene or 2-methylthiophene hydrogenation in the presence of PdS/Al<sub>2</sub>O<sub>3</sub> vs. contact time contain maxima.

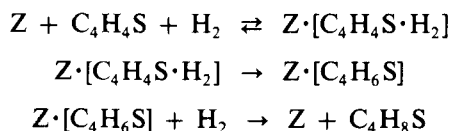
The selectivity towards thiolanes is close to 100% at low conversions and diminishes with increasing conversion degrees. For example, with 80% conversion of thiophene the selectivity is only 50% due to hydrogenolysis of thiolane (Figure 12). The reaction follows a parallel-consecutive scheme with predominance at  $T < 300^\circ\text{C}$  of the consecutive mechanism:



The hydrogenation rate rises with increasing thiophene concentration and partial pressure of hydrogen falls upon addition of thiolane. At constant hydrogen pressures and low conversion degree of thiophene the reaction rate is first order with respect to thiophene:

$$v = K \cdot C.$$

In the general case the inhibiting effect of the reaction product and the effect of the hydrogen pressure must be taken into account. It can be assumed that the liquid-phase hydrogenation of thiophene on PdS/Al<sub>2</sub>O<sub>3</sub>, like on other catalysts,<sup>141,142</sup> takes place via dihydrothiophene formation. On the active center of the catalyst there forms an intermediate thiophene-hydrogen adduct which then slowly transforms in the partly hydrogenated compound, i.e. dihydrothiophene. The latter is not an aromatic substance, hence it further hydrogenates to thiolane at a high rate and the resulting thiolane is desorbed from the surface:



Here Z is the active center of the catalyst and each of the above steps can be a sum of several fast steps, including those involving the adsorption of reactants. The kinetic equation deduced from the postulated scheme can be transformed as follows:

$$v = \frac{K \cdot C \cdot P_{H_2}}{a \cdot C_T}$$

Where  $K$  is the rate constant and  $C$  and  $C_T$  are the concentrations of thiophene and thiolane, respectively. This equation describes the experimental data fairly well.<sup>148</sup>

The reactivities<sup>154,165</sup> of thiophene and its homologs do not differ greatly and are close to those established for benzothiophenes (Table 21). This allows one to obtain thiolanes via hydrogenation of various thiophene-containing mixtures. In particular, it is possible to hydrogenate a mixture of thiophenes contained in mean distillates and gasoline fractions of petroleum, to thiacycloalkanes.

### III. CATALYTIC SYNTHESIS OF SULFOXIDES AND SULFONES

#### III.1. Oxidation of Sulfides to Sulfoxides and Sulfones

Sulfoxides and sulfones are obtained by the treatment of sulfides with various stoichiometric oxidants such as peroxides, hydroperoxides, nitric and chromic acid, nitrates, potassium persulfate, halogens, and permanganate.<sup>70,166-169</sup> The selective oxidation of sulfides with hydrogen peroxide and hydroperoxides is aided by the use of catalysts (compounds of tungsten, molybdenum, vanadium, titanium, zirconium,<sup>2,166,169</sup> and allows the production of sulfoxides and sulfones in high yields. More economic appears the use of molecular oxygen as a cheap and easily available oxidant.

**Table 21.** Hydrogenation of thiophenes in cyclohexane solution in the presence of alumopalladium catalysts<sup>154, 165</sup>

| Compound                   | T, °C | P <sub>H<sub>2</sub></sub> , MPa   | Concentration of thiophene, mol/l | Time, h | Yield of thiolane, mol. % |
|----------------------------|-------|------------------------------------|-----------------------------------|---------|---------------------------|
|                            |       | Pd/Al <sub>2</sub> O <sub>3</sub>  |                                   |         |                           |
| 2-Methylthiophene          | 200   | 8.5                                | 0.25                              | 1.0     | 36                        |
|                            | 260   | 5.0                                | 0.13                              | 0.25    | 56                        |
|                            | 260   | 5.0                                | 0.13                              | 0.5     | 67                        |
| 3-Propylthiophene          | 200   | 8.5                                | 0.19                              | 1.0     | 36                        |
| 2-Octylthiophene           | 200   | 8.5                                | 0.19                              | 1.0     | 59                        |
|                            |       | PdS/Al <sub>2</sub> O <sub>3</sub> |                                   |         |                           |
| 2-Methylthiophene          | 200   | 3.5                                | 0.13                              | 1.0     | 25                        |
|                            | 200   | 5.0                                | 0.13                              | 0.5     | 23                        |
|                            | 200   | 5.0                                | 0.13                              | 1.0     | 37                        |
|                            | 200   | 8.0                                | 0.13                              | 1.0     | 42                        |
| 2-Octylthiophene           | 200   | 5.0                                | 0.064                             | 0.5     | 32                        |
|                            | 200   | 5.0                                | 0.064                             | 1.0     | 41                        |
| 3-Hexylthiophene           | 200   | 8.5                                | 0.1                               | 0.5     | 42                        |
| 2-Butyl-5-methylthiophene  | 200   | 5.0                                | 0.1                               | 0.5     | 26                        |
|                            | 200   | 5.0                                | 0.1                               | 1.0     | 35                        |
| Benzothiophene             | 200   | 5.0                                | 0.1                               | 1.0     | 55                        |
| 3-Methylbenzothiophene     | 200   | 5.0                                | 0.09                              | 1.0     | 40                        |
| 3,6-Dimethylbenzothiophene | 200   | 5.0                                | 0.08                              | 1.0     | 53                        |
| Concentrate*               | 255   | 5.0                                | 0.1                               | 1.0     | 50                        |
| Diesel fuel                | 200   | 9.5                                | 0.03                              | 2.0     | 65                        |

\* hydrogenation in dodecane solution.

In the gas-phase oxidation of sulfides with oxygen unassisted by catalysts the yield of sulfoxides and sulfones is negligibly small; under these circumstances products of complete oxidation are mainly formed. The process follows a radical mechanism, via  $\text{RS}\dot{\text{C}}\text{H}_2$  and  $\text{H}\dot{\text{O}}_2$  radical formation and their subsequent transformations.<sup>2</sup> At atmospheric pressure the liquid-phase reaction starts at  $T \sim 75^\circ\text{C}$ , but occurs at a noticeable rate only upon addition of radical initiators.<sup>170</sup> An increase in pressure and temperature of the liquid-phase oxidation promotes the formation of sulfoxides. For example, the oxidation of dimethyl sulfide, decyl methyl sulfide, and thiolane with oxygen in aqueous alcoholic solution at  $100\text{--}130^\circ\text{C}$  and  $P \sim 7\text{ MPa}$  in the absence of catalysts yields 80–90% of sulfoxides; however, the process is slow (20–64 hrs).<sup>171</sup> Heating liquid dibutyl sulfide 1 h at  $120^\circ\text{C}$  and  $P = 5\text{ MPa}$  leads to less than 0.5 mol.% yield of sulfoxide; dibutyl sulfone is not formed.<sup>172</sup>

In the presence of solid oxide catalysts and at  $250\text{--}600^\circ\text{C}$  complete oxidation of sulfides to  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  takes place.<sup>173</sup> When assisted by homogeneous catalysts (nitrogen oxides), oxidation of sulfides to sulfoxides with oxygen occurs easily, but the process is technologically complex.<sup>2,166</sup>

Metal compounds have found wide use as catalysts of partial oxidation of various organic substances by oxygen. These catalysts are also appropriate for the mild oxidation of sulfides to sulfoxides and sulfones with oxygen. The reaction is carried out in the gas and the liquid phase.

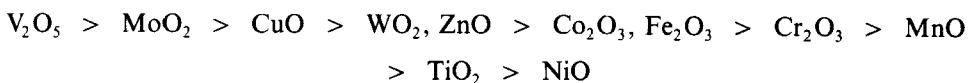
*III.1.1. Gas-phase oxidation of sulfides* Thorough studies of gas-phase oxidation of sulfides with oxygen have been described in.<sup>174–179,182–197</sup>

*III.1.1.1. Activity and stability of metal oxides* At temperatures below  $250^\circ\text{C}$  the reaction in the presence of V, Cu, Mn, and Mo oxides occurs only on the catalyst surface and does not proceed in the bulk; the oxidation products include sulfoxides and sulfones; products of a more complete oxidation, such as  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{COS}$ , aldehydes, carboxylic acids, and sulfonic acids as well as alcohols are also formed. At higher temperatures the gas-phase oxidation of sulfides in the presence of metal oxides follows a heterogeneous-homogeneous path resulting mainly in sulfide destruction.<sup>170,174,175</sup>

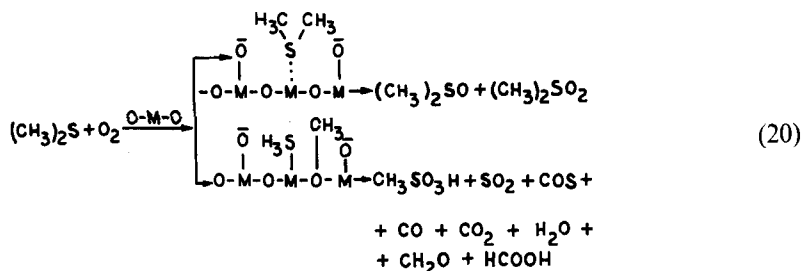
The oxidation of dimethyl sulfide with molecular oxygen at atmospheric pressure under conditions preventing reaction in the bulk has been studied most comprehensively.

The activity of metal oxides changes as a function of the nature of the catalyst.<sup>176–178</sup> Experiments in a flow-circulation system with constant-flow concentration of sulfide or with removal of products from the reaction mixture have indicated that the differences in catalytic activity are associated neither with the kinetic features of the dimethyl sulfide oxidation on various oxides nor with the poisoning of the surface by the reaction products in the gas phase.<sup>174</sup>

According to the rate of dimethyl sulfide oxidation per  $1\text{ m}^2$  of surface the oxides can be arranged in the same order relative to complete oxidation and formation of partial oxidation products (dimethyl sulfoxide and dimethyl sulfone):



The corresponding values characterizing the cation acceptor strength<sup>5,59</sup> and the ionization potentials change in the same order. This fact may be taken as evidence from the formation of a donor-acceptor bond between the sulfur atom and the cation during the chemisorption of the sulfide which results in its activation.<sup>57,58</sup>



For the mild oxidation reactions the quantitative correlation between the catalytic activity and values characterizing the acceptor strength is not satisfactory. One of the reasons may be an insufficient reliability of these latter values. Besides, it is possible that for the formation of sulfoxides and sulfones a complex of definite structure (*vide infra*) must be formed. Still more important seems to be the presence of surface active oxygen with a definite energy of binding to the catalyst in the vicinity of chemisorbed sulfide. For example, vanadium, copper, and manganese sulfate and sulfonates, which, like other salts, have less mobile oxygen on the surface than the corresponding oxides,<sup>180</sup> are almost without effect upon the formation rate of sulfoxides and sulfones.<sup>5,177</sup> It seems likely that for high catalyst activity in mild oxidation, the surface oxygen should have a moderate binding energy, as is the case for the most active compound,  $\text{V}_2\text{O}_5$  (ca. 180 kJ/mol).<sup>179,181</sup>

Variations in the energy of the oxygen binding to the surface have no effect on the catalytic activity in complete oxidation reactions. In particular, sulfates and sulfones possess activities equal to those of oxides.<sup>5</sup> There is a correlation between the activities of oxides in the sulfide decomposition reaction in the presence of oxygen and in inert media. For the latter case the rate-determining step has been found to be the decomposition of the surface complex.<sup>105</sup>

Most probably the complete oxidation products are formed as a result of interaction of chemisorbed fragmentary species of sulfide with either surface or molecular oxygen, and the rate-determining step of the process is the decomposition of the surface sulfide complex at the C-S bond.<sup>5</sup>

*Catalyst stability.* In the mild oxidation of dimethyl sulfide metal oxides remain stable for some time; however, upon prolonged operation they tend to deactivate.<sup>177</sup> In this latter instance, sulfur and carbon can be detected on the surface and their content increases with increasing duration of the experiment. On the surface there is mainly sulfonate sulfur as well as small amounts of sulfate sulfur;<sup>183</sup> IR spectra of the deactivated catalyst exhibit absorption bands at 1210, 1180, and 1050  $\text{cm}^{-1}$  corresponding to  $\text{SO}_4^{2-}$  and at 1260 and 3020  $\text{cm}^{-1}$  ascribed to sulfonate species.<sup>103</sup>

Catalyst deactivation occurs under the action of the products of complete oxidation of the sulfide.<sup>183-185</sup> Sulfur dioxide is a weaker poison than sulfonic acids. During the oxidation of sulfides at temperatures below 200 °C the formation of transition-metal

sulfates proceeds very slowly. Catalyst treatment with  $\text{SO}_2$  or  $\text{SO}_2$  introduction into the reaction mixture leads to very little deactivation; substitution of a sulfonic acid for  $\text{SO}_2$  leads to a dramatic decrease in catalytic activity. Metal sulfates and sulfonates are inert towards mild oxidation. IR studies have shown<sup>183</sup> that during chemisorption of dimethyl sulfide on oxides various surface species are formed. Some of these surface species, i.e. sulfide, sulfoxide, and sulfone, desorb at temperatures below  $200^\circ\text{C}$ . Desorption of other species such as carboxylates, sulfonates, and sulfates occurs at above  $450^\circ\text{C}$  with simultaneous partial destruction.

The catalyst deactivated during the course of dimethyl sulfide oxidation contains "organic sulfur" in amounts 2–3 orders of magnitude ( $0.2\text{--}2\text{ mmol/m}^2$ ) larger than the maximum possible amount formed by chemisorption of sulfide, sulfoxide, or sulfone ( $2 \cdot 10^{-3}\text{ mmol/m}^2$ ). During the time where the activity of vanadium, copper, cobalt, iron, and chromium oxides in the partial oxidation at  $185^\circ\text{C}$  and  $\tau = 5\text{ s}$  decreases by a factor of 2 in comparison with the initial activity nearly the same amount of dimethyl sulfide ( $0.5\text{--}0.8 \cdot 10^{-3}\text{ mol per } 1\text{ m}^2$ ) is converted to the products of complete oxidation.

The higher the rate of destruction of the initial sulfide the faster is the fall of activity in the mild oxidation. The rate of destruction of dimethyl sulfide increases with increasing temperature and contact time.<sup>183,185</sup>

The above results point to an important role of the complete oxidation products in the catalyst deactivation process and indicate that the different oxides are probably deactivated by interaction with the same poison. The content of sulfonate sulfur in the catalysts indicated above is  $0.001\text{--}0.002\text{ g S/m}^2$ . The content of products of mild oxidation (P) formed per  $1\text{ m}^2$  of the surface of active oxide is higher than on catalysts of low activity. The phenomenon observed here can be accounted for by the fact that P is determined by the ratio between the rate of useful product formation ( $v$ ) and that of catalyst deactivation which depends upon the rate of the appearance of the poison ( $v_p$ ) and that of its interaction with the catalyst ( $v_{\text{ads}}$ ):

$$P = v/v_p + v_{\text{ads}}$$

The  $v_{\text{ads}}$  of acid products on different oxides is high ( $2 \cdot 10^{-4}\text{ g S/m}^2$ ) and significantly exceeds the reaction rate;  $v_p$  is proportional to the rate of destructive transformation of the initial compound. Regarding the rate of destructive oxidation of dimethyl sulfide the oxides differ within one order of magnitude, while they differ more strongly with regard to the rate of partial oxidation.

Removal of only the sulfate sulfur from the catalyst does not restore its activity. The catalyst can be completely regenerated only after removal of the sulfonate sulfur. In the oxidative medium part of the sulfonate decomposes to form sulfate.<sup>177</sup>

One may conclude that the main reason for oxide deactivation in the partial oxidation of dimethyl sulfide is the formation of the surface sulfonate.<sup>103,177,183</sup> Most probably this results from the dissociative chemisorption of the sulfide as well as from the interaction of the catalyst with the product of complete oxidation, the sulfonic acid.

In the oxidative medium the surface sulfonate can convert into surface sulfate which is also inert towards mild oxidation. There is thus a possibility for the formation of a  $\text{R}_2\text{S} \rightarrow \text{M} \leftarrow$  complex since sulfate and sulfonate groups cannot react with all oxide cations due to steric hindrance; consequently, the sulfoxide or sulfone can form. However, the number of active surface sites and their accept or strength tend to decrease



under the action of chemisorbed poisons. Of special importance is the fact that after sulfurization yielding sulfate and sulfonate groups the binding of the oxygen to the surface becomes stronger and its reactivity falls. These events may hinder the partial oxidation process. As has been noted, the complete oxidation reaction is limited by the decomposition of the surface sulfide complex at the C–S bond;<sup>5</sup> therefore catalyst desulfurization during operation has no effect on the catalytic activity.

To increase the stability of catalysts for the selective oxidation of sulfides to sulfoxides or sulfones the process should be carried out under conditions preventing the formation of sulfate and sulfonate groups, i.e. at the lowest temperatures and shortest contact times possible. On reduced (under the action of sulfide) catalysts extensive chemisorption of poisons takes place. During operation with substoichiometric amounts of oxygen the stability of transition-metal oxides is considerably lower than in contact with excess oxygen.<sup>182,183,185,186</sup> Therefore, in the presence of these catalysts the synthesis of sulfoxides and sulfones should be carried out with a large excess of oxygen in the system.

Catalysts deactivated in oxidation processes can usually be regenerated by treatment with oxygen at elevated temperatures. With oxide catalysts for the partial oxidation of sulfides such a treatment is excluded because the resulting sulfates are difficult to convert to oxides (with the exception of vanadyl sulfate). The regeneration of catalysts in inert media under conditions providing desorption of undecomposed sulfonate species from the surface leads to a complete recovery of the activity of the catalyst. Vanadium oxide catalysts can be regenerated in oxidative media.<sup>186</sup> Depending on the composition of the vanadium catalyst, regeneration is necessary after 100–200 g of dimethyl sulfoxide have been formed per 1 kg of  $V_2O_5$ .

The specific activity of  $V_2O_5$  supported on corundum, pumice, or glass is close to that of bulk  $V_2O_5$ ;  $\gamma$ - $Al_2O_3$  based catalysts are unselective; the specific activity of vanadium silicate catalysts is lower than that of  $V_2O_5$ . The best supports for  $V_2O_5$  are silicalite, corundum, and titania.<sup>186,187</sup> Modification of  $V_2O_5$  with additives (phosphorus, chromium, iron, cobalt, copper, molybdenum, tungsten, silver, tin, antimony, lead, bismuth, etc.)<sup>188</sup> has little effect on the activity and selectivity of the catalyst. In the presence of  $V_2O_5$  containing a copper additive the selectivity towards sulfoxide increases from 65–70% to 80–85%.

It cannot be ruled out that the high selectivity of copper-vanadium catalysts towards sulfoxide formation is associated with the presence of a certain state of copper in them. In this respect some copper-containing catalysts have been examined.<sup>189</sup>

In the presence of  $CuO/SiO_2$  at 130–190 °C and  $\tau = 6$ –18 s in the gas phase destructive oxidation of dimethyl sulfide takes place with the evolution of  $SO_2$ ; no partial oxidation products are formed. On  $SiO_2$ -supported copper acetylacetonate destruction of sulfide with the evolution of  $SO_2$  does practically not occur. The oxidation products contain dimethyl sulfoxide, however, its yield does not exceed 2 mol.%. Far more active in partial oxidation is  $CuCl_2/SiO_2$  in the presence of which under the above conditions the yield of dimethyl sulfoxide reaches 26 mol%; dimethyl sulfone is also formed, the selectivity being, respectively, 70–85 and 15–30%. The observed difference in activity is due to the type of sulfide complex formation with the copper-containing catalyst. As ascertained by NMR,<sup>189</sup> the interaction of the gaseous sulfide with  $CuCl_2/SiO_2$  gives rise to a surface complex with sulfide ligands. The sulfide coordinates to  $SiO_2$ -supported copper oxide or acetylacetonate by entering the axial plane without noticeable electron density transfer to the copper ion and to  $CuCl_2/SiO_2$  by entering the equatorial plane of



The rates of formation of the reaction products and the total conversion of the sulfide are independent of the oxygen concentration and tend to increase with increasing concentration of dimethyl sulfide. Water (at concentrations above 0.05 vol.%) and the sulfoxide (at concentrations above 0.08 vol.%) inhibit the process. The total reaction rate and the rates of formation of the sulfoxide, the sulfone, and of the destruction products can be described as

$$v = \frac{K \cdot P_S}{1 + b_1 \cdot P_{SO} + b_2 \cdot P_{H_2O}}$$

Since at conversions of dimethyl sulfide from 10 to 15% sulfoxide and H<sub>2</sub>O do not inhibit the process, the equation for the oxidation rates transforms to a first-order equation with respect to dimethyl sulfide:

$$v = K' \cdot P_S$$

The activation energy of dimethyl sulfide oxidation over V<sub>2</sub>O<sub>5</sub> is 26 kJ/mol and those of dimethyl sulfoxide and dimethyl sulfone formation are, respectively, 20 and 34 kJ/mol.

The principles of the oxidation of sulfides of different structure on V<sub>2</sub>O<sub>5</sub> are similar to those of the oxidation of dimethyl sulfide,<sup>192-195</sup> i.e., at low conversions of the sulfide only the sulfoxide and the sulfone are formed via independent paths; under more rigid conditions overoxidation of the sulfoxide to the sulfone and formation of destruction products take place (cf. p. 343).

The destructive oxidation of high-molecular weight sulfides begins at lower conversions than for dimethyl sulfide and proceeds at a higher rate.

A given sulfoxide is oxidized on V<sub>2</sub>O<sub>5</sub> with a quantitative yield of the sulfone. The presence of the sulfide which is predominantly adsorbed on the catalyst hinders the oxidation of the sulfide to the sulfone.

At sulfide conversions of up to 15% the oxidation is described by an equation which is first order with respect to the sulfide. The activation energy of the partial oxidation of various sulfides is close to that for dimethyl sulfide, i.e. 25-29 kJ/mol. However, with increasing molecular weight of the sulfide during the oxidation on V<sub>2</sub>O<sub>5</sub> the contribution of complete oxidation increases due to easy dissociation of chemisorbed sulfide accompanied by C-S bond rupture.

Different mechanisms can be proposed for the description of the formation of products of partial oxidation of sulfides by molecular oxygen.

The sulfoxide and the sulfone may be formed from a sulfide either due to direct interaction of the sulfur atom with oxygen or to a radical-chain process via proton abstraction from the  $\alpha$  carbon atoms or via dissociation of the starting sulfide at a C-S bond. For the oxidation over V<sub>2</sub>O<sub>5</sub> the choice between these mechanisms of the formation of sulfoxides and sulfones has been made<sup>5,59,178,193,194</sup> by comparison of the product composition in sulfide oxidation and of the rates of their formation. It has been established that at low conversions (up to 15%) the rate of dimethyl sulfide oxidation is much higher than that of the oxidation of phenyl methyl sulfide and of benzyl methyl sulfide. When the reaction occurs  $\alpha$ -proton abstraction in inverse dependence should be observed. Moreover, also compounds such as di-*t*-butyl and diphenyl sulfide, which do not contain  $\alpha$ -hydrogen atoms, are oxidized to yield sulfoxides and sulfones, although the differences in the energies of bond rupture and the dipole moments are insignificant (Table 22). The oxidation of asymmetric sulfides gives only the sulfoxide (sulfone) with

**Table 22.** Oxidation of sulfides in the presence of  $V_2O_5$ <sup>194</sup>

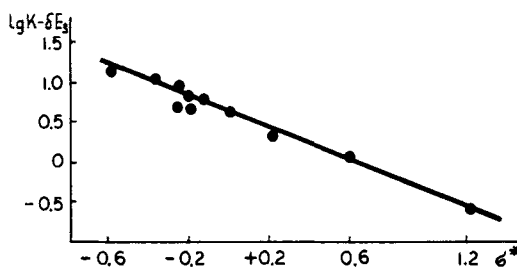
| Sulfide  | K<br>(mmol/m <sup>2</sup> ·h)<br>190 °C | E<br>kJ/mol) | $\mu$<br>(D) | U<br>(eV) | F <sub>r</sub> | q     |
|--|---|--------------|--------------|-----------|----------------|-------|
| (CH <sub>3</sub> ) <sub>2</sub> S                              | 4.46                                    | 306          | 1.40         | 8.77      | 1.043          | 1.974 |
| (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S                | 2.75                                    | 297          | 1.61         | 8.56      | 1.045          | 1.974 |
| (C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> S                | 1.48                                    | 302          | 1.55         | 8.45      | 1.045          | 1.975 |
| (CH <sub>3</sub> CH) <sub>2</sub> S                            |   |              |              |           |                |       |
|  | 1.62                                    | 293          | —            | 8.38      | —              | —     |
| CH <sub>3</sub>  |   |              |              |           |                |       |
| (C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> S                | 1.37                                    | 306          | 1.57         | 8.40      | 1.045          | 1.975 |
| (CH <sub>3</sub> CHCH <sub>2</sub> ) <sub>2</sub> S            |   |              |              |           |                |       |
|  | 0.66                                    | —            | —            | 8.36      | —              | —     |
| CH <sub>3</sub>  |   |              |              |           |                |       |
| C <sub>4</sub> H <sub>9</sub> SC <sub>2</sub> H <sub>5</sub>   | 2.55                                    | 306          | —            | —         | 1.045          | 1.975 |
|  |   |              |              |           |                |       |
| CH <sub>3</sub>  |   |              |              |           |                |       |
| (CH <sub>3</sub> -C) <sub>2</sub> S                            | 0.10                                    | 276          | —            | 8.16      | —              | —     |
|  |   |              |              |           |                |       |
| CH <sub>3</sub>  |   |              |              |           |                |       |
| C <sub>6</sub> H <sub>5</sub> SCH <sub>3</sub>                 | 1.87                                    | 323          | 1.27         | —         | 0.953          | 1.950 |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>3</sub> | 1.03                                    | 222          | —            | —         | 1.005          | 1.964 |
| (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S                | 0.59                                    | 323          | 1.47         | —         | 0.844          | 1.913 |
| C <sub>4</sub> H <sub>8</sub> S                                | 1.77                                    | —            | 0.87         | 8.48      | —              | —     |

the intact skeleton of the initial sulfide, i.e. they are formed directly from the sulfide rather than from its decomposition products. The sulfoxide and the sulfone are the main reaction products which is hardly probable for a reaction proceeding via destruction of the initial sulfide, even in the case of a radical non-chain process. This reasoning allows one to conclude that the sulfoxide and the sulfone are formed by direct interaction of the sulfur atom with oxygen.

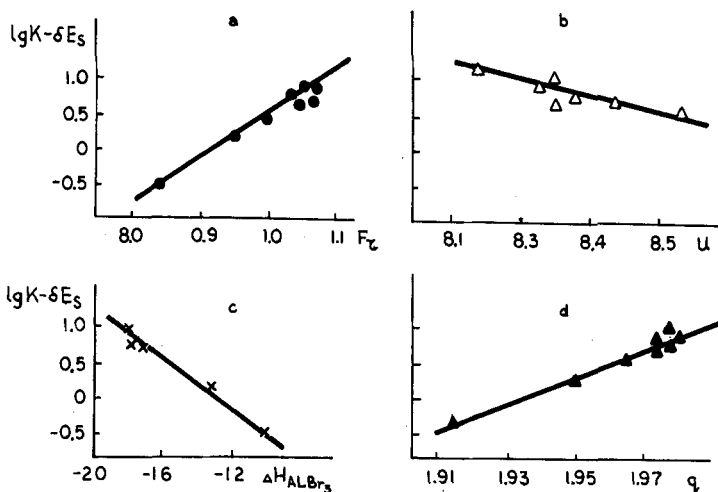
There exists a correlation between the rate of sulfide oxidation and the donor ability of the sulfur atom. Taking into account steric effects brought about by substituents (Figure 14) the correlation between the oxidation rate constants and the inductive constants of the Taft equation is as follows:

$$\lg k = 0.65 - 0.91\sigma^* + 0.52 E_s^0$$

Since  $\rho^*$  has a negative sign, the reaction under consideration is electrophilic, during



**Figure 14.** Correlation of the rate constants for the partial oxidation of sulfides with the inductive constants from Taft's equation and the steric substituent constants  $E_s$ .<sup>194</sup>



**Figure 15.** Correlation of the rate constants for the partial oxidation of sulfides with the index as of free valency (a), the ionization potentials (b), the enthalpy of formation of sulfide complexes with  $\text{AlBr}_3$  (c), and the surface charge of the sulfur atoms (d).<sup>194</sup>

which oxygen attacks the sulfur atom of the sulfide. This process is favored by substituents which enhance the electron density at the sulfur atom. The  $\rho^*$  value of  $-0.91$  indicates reaction this sensitivity.

There is also a relation between the rate constant ( $k$ ) and the reactivity indexes calculated by the MO method: ( $g$  = charge on the sulfur atom,  $F_r$  = index of free valency,  $m$  = position of the HOMO,  $C_r^2/m$  = Fukui index), the experimentally found ionization potentials ( $U$ ), the dipole moments ( $\mu$ ), the heat of formation of the donor-acceptor bonds in the sulfide complexes ( $\Delta H$ ), and the energy of the C-S bond cleavage ( $E$ ) (Table 22, Figure 15). The results obtained indicate that the reaction site is the sulfur atom whose interaction with oxygen leads to the formation of the sulfoxide and the sulfone.

The validity of the proposed mechanism is supported by adsorption and kinetic studies.

The kinetics of dimethyl sulfide chemisorption on a  $\text{V}_2\text{O}_5$  surface has been examined in.<sup>190,192</sup> On the reduced surface the adsorption is by a factor of 1.2 slower than on the oxidized surface. The limiting amount of dimethyl sulfide adsorbed on  $\text{V}_2\text{O}_5$  is  $(1-1.7) \cdot 10^{-6}$  mol/m<sup>2</sup>. At a surface coverage of about 1% of monolayer the heat of adsorption is  $17 \pm 4$  kJ/mol, which is lower than the activation energy of the oxidation. The rate of sulfide chemisorption is 2-3 orders of magnitude higher than the rate of oxidation and thus the chemisorption cannot be the rate-determining step of the sulfoxide or sulfone formation. The limiting amount of dimethyl sulfoxide adsorbed on  $\text{V}_2\text{O}_5$  is  $0.6 \cdot 10^{-6}$  mol/m<sup>2</sup>, i.e. of the same order as the amount of dimethyl sulfide. The desorption of the sulfoxide begins at 150 °C, and that of the sulfide at 100 °C, but some of the surface species first desorbs at 450 °C. The rate of oxygen adsorption on the reduced surface is far higher than the rate of sulfide oxidation.

The adsorption of dimethyl sulfide on  $\text{V}_2\text{O}_5$  is accompanied by its interaction with surface oxygen of the oxide to form the oxidation products. This fact follows<sup>58</sup> from

experiments on thermodesorption according to which  $(\text{CH}_3)_2\text{SO}$ ,  $(\text{CH}_3)_2\text{SO}_2$  and  $\text{SO}_2$  are formed, along with unchanged  $(\text{CH}_3)_2\text{S}$ . During the course of thermodesorption of  $(\text{CH}_3)_2\text{SO}$  adsorbed on  $\text{V}_2\text{O}_5$ ,  $(\text{CH}_3)_2\text{SO}_2$  and decomposition products are formed. Since these experiments on adsorption and desorption were made in inert media the oxygen-containing products undoubtedly result from the interaction of a chemisorbed state of dimethyl sulfide with oxygen of  $\text{V}_2\text{O}_5$ . In the IR spectra after adsorption of  $(\text{CH}_3)_2\text{S}$  on  $\text{V}_2\text{O}_5/\text{SiO}_2$  (as well as on  $\text{Cr}_2\text{O}_3$ ) weak absorption bands appear, along with others, which belong to  $(\text{CH}_3)_2\text{SO}$  and  $(\text{CH}_3)_2\text{SO}_2$  resulting, probably, from the interaction of the sulfide with surface oxygen.<sup>57</sup> Addition of oxygen to the cell after sulfide adsorption leads to an increase in the intensity of absorption bands ascribed to dimethyl sulfide oxidized at the sulfur atom. The appearance of these states on the oxidized surface of the oxide seems to occur with participation of oxygen adsorbed on the oxide, because their appearance is accompanied by a decrease in the intensity or even disappearance of the absorption bands of oxygen.

When  $(\text{CH}_3)_2\text{S}$  is passed through  $\text{V}_2\text{O}_5$  in an inert atmosphere  $(\text{CH}_3)_2\text{SO}$  is formed with a selectivity close to that observed for the reaction in an oxygen atmosphere. From all of the above one may conclude that the partial oxidation of dimethyl sulfide follows a redox pattern.

The first step of the formation of dimethyl sulfoxide is assumed to be the adsorption of dimethyl sulfide on the oxidized surface of  $\text{V}_2\text{O}_5$ . The dimethyl sulfide interacts with the surface oxygen and thus is oxidized to the sulfoxide bound to the reduced surface. The sulfoxide is desorbed and the reduced catalyst sites become free. These sites are reoxidized by oxygen. Dimethyl sulfide is adsorbed on reduced sites and dimethyl sulfoxide reduced on oxidized surface sites. The sulfone and the products of destructive oxidation formed on other sites also adsorb on the sites which are active in the oxidation of the sulfide to the sulfoxide.

It has been recommended<sup>186</sup> that the oxidation of dimethyl sulfide to dimethyl sulfoxide should be carried out at small conversions of the sulfide (up to 50%) under conditions where products of destructive oxidation do not form: at 160–200 °C and a content of the sulfide in oxygen of up to 1% by volume (the lowest limit of combustibility). Unreacted dimethyl sulfide having a lower boiling point than the oxide can easily be isolated from the mixture and recycled. The process can be effected in a flow reactor with a fixed bed of a periodically regenerated catalyst or, even better, in a continuous process in a fluidized catalyst bed with catalyst circulation in the reactor-regenerator system.

### III.1.2. Liquid-phase oxidation of sulfides

**III.1.2.1. Heterogeneous oxidation** The partial oxidation of dibutyl sulfide with oxygen has been examined<sup>197–200</sup> in the liquid phase at  $T = 70\text{--}140\text{ }^\circ\text{C}$ , 5 MPa, a reaction time of 1–3 h, and without solvent in the presence of solid catalysts: metals, sulfides, oxides. In the presence of  $\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5\text{--MoO}_3$ ,  $\text{V}_2\text{O}_5\text{--WO}_3$ ,  $\text{MnO}_2$ , the sulfoxide and the sulfone are formed in 25–40 mol.% and 2–4 mol.% yield, respectively. Less active are Bi, Mo, Co, and Cu oxide; hardly active are NiS,  $\text{Re}_2\text{S}_7$ , CuS,  $\text{WS}_3$ , MnS, and metallic Pt and Ag. In the presence of 5%  $\text{Ru/Al}_2\text{O}_3$  at 105 °C and 7 MPa dibutyl sulfide in benzene solution is selectively oxidized<sup>200</sup> to form 44% dibutyl sulfoxide and 9% of the sulfone,

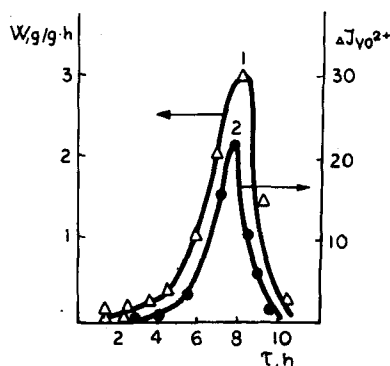
but for the achievement of such yields the reaction must be performed for 12 h. Thus, transition-metal oxides are most active.

The productivity of some oxides with respect to sulfoxide and sulfone is very high.<sup>106,196,201-204</sup> However, even at low temperatures the oxidation of dibutyl sulfide is accompanied by the formation of the disulfide, the sulfonic acid, the aldehyde, the carboxylic acid, water, sulfate, sulfonate, sulfinate, and sulfur dioxide. Thus the composition of the products does not differ from that for the oxidation of sulfide in the presence of a radical initiator such as azobisisobutyronitrile. The formation of the side products seems to be due to cleavage of sulfide C-S bonds and is difficult to explain in any other way.

During the oxidation an induction period is observed and the time dependence of the rate has a maximum (cf., e.g., Figure 16). The maximum rate of the oxidation of dibutyl sulfide on  $V_2O_5$  increases proportionally with the concentration of the sulfide and  $[V_2O_5]^{1/2}$  and is independent of the oxygen concentration. 1-Naphthol inhibits the process. These results indicate that the oxidation of the sulfide in the liquid phase in the presence of metal oxides follows a radical chain mechanism. This chain process seems to develop due to the initiation effect of solid catalysts;<sup>205</sup> the products formed on the catalyst surface can easily migrate into the bulk.<sup>206</sup>

After oxidation of dibutyl sulfide in the presence of Mo, Cr, Mn, Ti, and Zn oxide, the corresponding metal ions cannot be detected in the solution. The rate does not change upon addition of reaction products capable of coordination to these metal ions. Consequently, in the presence of these catalysts a heterogeneous oxidation takes place. Solid catalysts seem to have an initiation effect.

The products obtained by oxidation of dibutyl sulfide in the presence of vanadium or copper oxide contain  $VO^{2+}$  or  $Cu^{2+}$  ions, as demonstrated by ESR, IR, and chemical analysis. The plots of the ion concentration in the oxidized reaction mixtures versus the reaction time are identical with the kinetic curves for the oxidation in the presence of oxides (cf., e.g., Figure 16).  $VO^{2+}$  ions appear in solution almost from the very beginning of the reaction, their formation being most facile when lower-valence vanadium oxides



**Figure 16.** Liquid-phase oxidation of dibutyl sulfide over  $V_2O_5$  at  $100^\circ C$  and  $P = 5 \text{ MPa}$ .<sup>201</sup> 1 — formation rates of dibutyl sulfoxide ( $v$ , g sulfide/g cat · h); 2 — relative intensity of the EPR signals of vanadyl ions in oxidates.<sup>201</sup>

are used. The addition of 5% sulfone to the reaction mixture ( $T = 130^\circ\text{C}$ ,  $\tau = 1\text{ h}$ ,  $\text{V}_2\text{O}_4$ ) has no effect on the reaction, while addition of the sulfonic acid suppresses the reaction; the addition of the sulfoxide or of the carboxylic acid leads to a significant increase in the rate of the oxidation of the sulfide:

|                       | Sulfide conversion, % | Yield of sulfoxide, mol. % |
|-----------------------|-----------------------|----------------------------|
| Without additives     | 2.3                   | 1.4                        |
| Dibutyl sulfoxide     | 54.0                  | 22.2                       |
| Butyric acid          | 44.7                  | 22.4                       |
| Dibutyl sulfone       | 3.0                   | 1.6                        |
| 1-Butanesulfonic acid | 0.0                   | 0.0                        |

It seems likely that with vanadium or copper oxides as catalysts the reaction only begins on the surface, but then mainly a homogeneous sulfide oxidation occurs under the action of ion dissolved in the reaction mixture.

In acetone solution copper-containing aerosils (0.1–4 wt.% Cu) obtained by direct contact of aerosil with amine-copper complexes<sup>207</sup> are active and selective catalysts of diethyl sulfide oxidation. At  $T = 140^\circ\text{C}$ , 6 MPa, and a concentration of diethyl sulfide in acetone of 0.4–0.5 M with 0.2 M AcOH additive the selectivity towards diethyl sulfoxide is close to 100%. In the oxidized reaction mixture the copper ions detected amount to 30–50% of the initial copper content in the catalyst.  $\text{Cu}^{2+}$  ions are eluted with acetic acid and the sulfoxide is formed. The ions are washed off most easily from the surface of solid catalysts with a high copper content. Possibly, the oxidation reaction begins under the action of the solid copper-containing catalyst, but then it follows mainly a homogeneous path involving  $\text{Cu}^{2+}$  ions eluted from the surface.

An analysis of the ESR spectra<sup>207</sup> indicates that the copper ions on the surface of the aerosil are spaced at a distance where spin-spin interaction is possible, they can also occupy individual sites without interaction; the proportion of these sites tends to increase with decreasing copper concentration on the support. These sites are strongly bound to the surface and determine the activity of the heterogeneous catalyst. The contribution of the heterogeneous process in the case of catalysts with a high copper content is not large, since under the influence of the reaction mixture copper ions are eluted from the surface and a homogeneous sulfide oxidation occurs in the solution.

*III.1.2.2. Homogeneous-catalytic oxidation* Homogeneous oxidation of sulfides occurs in the presence of transition-metal complexes.

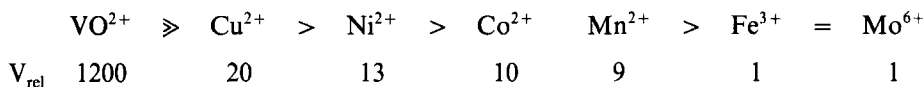
The oxidation of methionine by oxygen in aqueous solution in the presence of  $\text{HAuCl}_4$  has been described in.<sup>208</sup> Based on a kinetic study the reaction is assumed to occur via a methionine- $\text{Au}^{3+}$  complex, the rate-determining step being that of complex decomposition to sulfoxide and  $\text{Au}^+$ .

The oxidation of dibutyl sulfide has been studied<sup>196,209</sup> at  $120^\circ\text{C}$ , 5 MPa, and without solvent in the presence of halides, sulfates, acetates, butyrates, stearates, acetylacetonates, phthalocyanines, and some other complexes of VO, Cu, Co, Ni, Mn, Fe, Mo, Cr, Pb, and Rh. The activity of the above complexes in partial oxidation depends upon the nature of the metal and the type of ligand in the initial catalyst. The yield of dibutyl sulfoxide in the presence of vanadium or copper complexes amounts to 20–30 mol% per



1–3 h; other complexes are significantly less active; e.g., for Co, Ni, Mn, and Fe complexes the yield does not exceed 1–3 mol.% per 3 h.

According to the catalytic activity ( $v_{rel}$ , mol/g-ion·l·h at 120 °C) towards sulfoxide formation the metal acetylacetonates can be arranged in the following order:

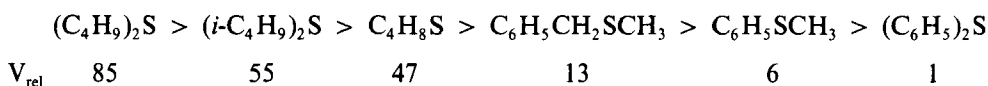


Vanadyl complexes, in which the vanadium atom is surrounded by oxygen atoms and a vacant site located axially relative to the vanadyl oxygen (such as the acetylacetonate, the sulfate, the carboxylates such as the acetate, the butyrate, the oxalate, and the resinate) are also active. At 100–150 °C, elevated air pressure and a reaction time of 1–3 h in the absence of solvent these complexes accelerate the oxidation of dialkyl sulfides, alkyl aryl sulfides, thiolane, and thiacycloalkanes to sulfoxides with a selectivity of 40–60%. As a result, a complex mixture of products is formed, the molar ratio of the products being the same as in the presence of AIBN. The process is inhibited by 1-naphthol, water, dibutyl disulfide, and 1-butanefulfonic acid and accelerated by butanol and dibutyl sulfoxide.<sup>196,209,210</sup>

The maximum yield of the sulfoxide in dibutyl sulfide oxidation is about 35 mol.% and remains unchanged with varying temperature, pressure, and reaction time. The reaction order with respect to the catalyst is close to 1/2, which is typical for processes subject to biradical chain termination.

Under the action of vanadyl acetylacetonate at 120 °C and 5 MPa thiacycloalkanes in diesel fuel are oxidized to the corresponding sulfoxides in a yield of up to 30 mol.% and with a selectivity of 50%.

In the presence of VO(acac)<sub>2</sub> the rate of oxidation decreases upon going from aliphatic to aromatic substitution of the sulfide sulfur



The reactivity of the sulfides is determined by the inductive effect of the substituents on the sulfur atom serving as the oxidation site. The first step of the process seems to be the formation of a bond between the sulfur atom and the vanadyl complex.

As follows from calculations, in the case of vanadyl acetylacetonate quite an efficient overlapping of a metal d-orbital with the sulfur 3p<sub>z</sub>-orbital is possible; in other words, a complex of the donor-acceptor type  $[\text{O}=\overset{\text{V}}{\text{X}} \leftarrow \text{:S} \overset{\text{R}}{\text{R}}]$  is formed.

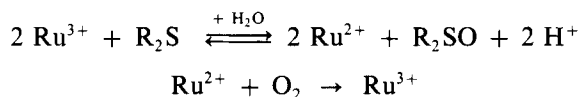
In this instance, as follows from ESR spectra of the oxidation products registered at various reaction times, the intensity of the signal ascribed to VO<sup>2+</sup> does not change, i.e. the valency of the vanadium remains unchanged. It is known<sup>211</sup> that vanadyl-oxygen complex cannot participate in one-electron interactions and therefore are hardly reducible. It is assumed that an unshared electron pair of the sulfide sulfur atom is donated to the vanadium as the complex forms which promotes the subsequent cleavage of a C–S bond and the appearance of R· and RS· radicals. The chain is propagated by peroxide radicals RO<sub>2</sub>· formed in the oxidative medium and the chains are terminated by radical recombination.

The initial composition of the complex changes during the experiment. In a deac-

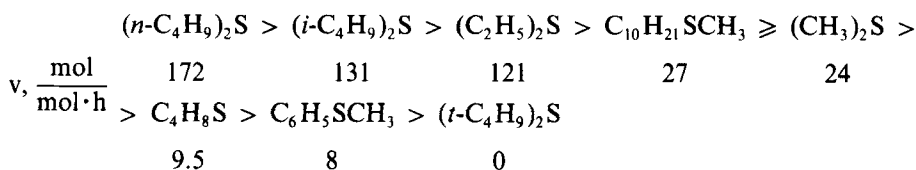
tivated complex the  $\text{VO}^{2+}$  ion is bound to a sulfonate group, as follows from the ESR spectra of the vanadyl complexes.

The selectivity towards the sulfoxide in the presence of the vanadyl complex increases when the reaction takes place in solvents, especially in acids, and reaches 70–80% at a maximum sulfoxide yield of 40%. The catalyst productivity with respect to the sulfoxide does not exceed 50 mol/mol cat. per h.

The rate of the homogeneous oxidation of sulfides assisted by different catalysts tends to increase when the reaction is performed in alcohols or benzene. Refs.<sup>212-214</sup> report on the oxidation of dibutyl sulfide dissolved in benzene or alcohols in the presence of various metal complexes. At 50–250 °C, 1–10 MPa, reaction time 12 h, and a sulfide-to-catalyst molar ratio of (22–44): 1, Cr, Mn, Co, Rh, Ni, Pd, and Pt chloride are inert towards the formation of partial oxidation products; Ir, Au, and Fe complexes are of very low activity; in the presence of Cu, Os, and Ru complexes dibutyl sulfoxide is produced in 10–35 mol.% yield and with 47–100% selectivity. With  $\text{RuCl}_3$  at 100 °C and 3.5 MPa, along with the sulfoxide, the sulfone is also formed in 76 mol.% yield. The yields of the sulfoxide and the sulfone decrease with increasing temperature. All catalysts tested are of low productivity. The reaction on Ru complexes is supposed to follow a redox mechanism:



The oxidation of sulfides of different structure has been carried out in the presence of complexes of Ru halides with dimethyl sulfoxide in methanol or 2-propanol.<sup>214</sup> The total selectivity towards the sulfoxide and the sulfone is about 100%. The reaction rate increases with increasing concentrations of catalyst, alcohol (to a certain extent), and oxygen and is independent of the concentration of the sulfide. A two-electron redox reaction has been postulated; according to this  $\text{Ru}^{2+}$  is oxidized by oxygen to  $\text{Ru}^{4+}$  with simultaneous formation of peroxide which oxidizes the sulfide to the sulfoxide. The solvent (alcohol) takes part in the regeneration of the catalyst. The productivity of Ru catalysts reaches up to 170 mol. sulfoxide per 1 g-ion Ru per h. With regard to their reactivity the following sulfides dissolved in methanol (0.15 M) and studied at 105 °C, 0.7 MPa, and a concentration of *trans*- $\text{RuBr}_2 \cdot (\text{CH}_3)_2\text{SO}$  of 1.5 mM obey the order:



Di-*t*-butyl sulfide is not oxidized under these conditions, and the oxidation of diisopropyl and of di-*sec*-butyl sulfide occurs via the secondary C–H bond rather than via the sulfur atom.

A slow oxidation of 1-decyl methyl sulfide by oxygen takes place in benzene solution

under the action of a bis(diphenyl sulfide) Ru complex capable of coordinating and activating oxygen.<sup>215</sup>

A homogeneous catalytic oxidation of sulfoxides to sulfones has been reported in.<sup>216</sup> E.g., in aqueous propanol at 100 °C dimethyl sulfoxide is oxidized to the sulfone under the action of Rh and Ir chloride, the yield being 20–90%. In aqueous solutions containing Cu, Pd or Fe chloride at 130–200 °C and 5 MPa the yield of the respective sulfone from dimethyl sulfoxide or thiolane 1,1-oxide was 26–36 mol.%. Far less active were Mn, Ni, Cr, Co, and VO chloride. The reaction occurs via the coordination between the sulfoxide and the catalyst metal atom.

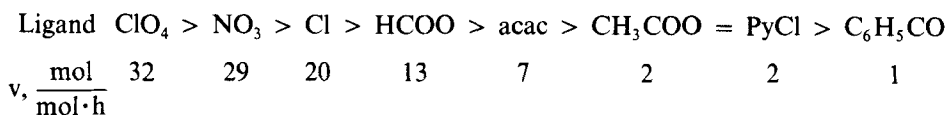
Heteropolyacids of the general formula  $H_{3+H}PMo_{12-n}V_nO_{40}$  ( $n = 1-6$ ) at  $T = 100-150$  °C and an oxygen pressure of 0.9–1.2 MPa in acetic acid, 2-propanol or acetone with addition of 5% water speed up the oxidation of dialkyl sulfides ( $R = C_1-C_4$ ) to the corresponding sulfoxides and sulfones.

The heteropolyacid with  $n = 6$  is most active. It is assumed that the reaction follows a redox mechanism with variable V valencies and reoxidation of the reduced form of the heteropolyacid by oxygen.<sup>217</sup> At low conversion of sulfide the selectivity towards the partial oxidation products reaches 100%, but the productivity is rather low, i.e. does not exceed 10 mol of sulfoxide per mol of catalyst per h. The low yield of sulfoxide and sulfone, and the need for large amounts of acid catalyst which is difficult to separate from the products make this method impractical for preparative purposes.

The oxidation of sulfides assisted by copper catalysts has been studied in detail.

In aqueous alkaline solutions in the presence of  $CuCl_2$ , aliphatic sulfides with  $R = C_2-C_{11}$  dissolved in hydrocarbons are oxidized by air at  $T = 60-160$  °C to the sulfones, but with a low selectivity, sulfonic acids and sulfate being formed in large amounts.<sup>218</sup>

More selective towards sulfoxides and sulfones are copper compounds in the oxidation of sulfides in neutral media. In the absence of solvent the oxidation of dibutyl sulfide has been studied at 120 °C and 5 MPa in the presence of copper chloride, nitrate, perchlorate, formate, acetate, benzoate, acetylacetonate, or pyridinate.<sup>209</sup> According to their relative activity towards sulfoxide formation the catalysts follow the order:



A kinetic study of dibutyl sulfide oxidation in the presence of  $CuCl_2$  at 100–130 °C, 3–5 MPa, and  $[CuCl_2] = 0.03-0.44$  M indicate that the rate of sulfoxide formation increases proportionally with the concentration of the catalyst and of the sulfide and is independent of the air pressure. The maximum yield of sulfoxide is 70 mol.%, the selectivity 80–90%, the productivity low (2 mol/mol·h), and the sulfoxides contain resinous contaminants.

The formation of partial oxidation products is facilitated by solvents.<sup>209,219</sup> In 2-propanol solution at  $T = 130-150$  °C and  $[CuCl_2] = 0.044$  M during 2–5 h dibutyl sulfide, thiolane, hexylthiolane, and thiacyclohexane are oxidized to the corresponding sulfoxides

in 60–70 mol.% yield and with a selectivity of up to 75%. The rate of oxidation of thiacyclohexane is ca. a factor of 2 lower than that of the other compounds. The productivity does not exceed 4 mol/g-ion Cu·h. Under the reaction conditions the 2-propanol is partially oxidized to acetic acid, acetone, diisopropyl ether, and carbonyl compounds. The sulfide oxidation products contain sulfones, sulfonic acids, and resin, along with sulfoxides.

The process is accelerated when acetic acid is used as a solvent.<sup>189,209</sup> The reaction rate is independent of the oxygen pressure over the range of 5 to 7 MPa and increases with increasing initial concentration of sulfide from 0.07 to 0.26 M (first order with respect to sulfide) and proportionally with the CuCl<sub>2</sub> concentration within the range 0.01–0.05 M. The complete oxidation of the sulfide at T = 100–150 °C is accomplished in several minutes; however, the sulfoxide produced contains much tar.

Copper catalysts in acetone solution have been found to be the most efficient in the oxidation of sulfides.

Dialkyl sulfides R<sub>2</sub>S (R = C<sub>1</sub>–C<sub>5</sub>), thiacyclohexane, thiolane, and its homologs are oxidized to the corresponding sulfoxides with 100% selectivity at T = 80–150 °C, 2–8 MPa, [CuCl<sub>2</sub>] = 1–60 mM, [sulfide] = 0.1–0.8 M, and reaction times of 5–60 min. Similar results have been obtained with copper bromide (Table 23).<sup>220</sup> The productivity of the catalysts with respect to the sulfoxides is higher by 2–3 orders of magnitude than that of other known catalytic systems for similar reactions (*vide supra*).

The formation of sulfoxides and sulfones can be accelerated not only by copper halides CuX<sub>2</sub> (X = Cl, Br) but also by some other Cu<sup>2+</sup> compounds:<sup>221</sup> carboxylates (RCOO)<sub>2</sub>Cu with R = CH<sub>3</sub>, NH<sub>2</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>COO; *o*- and *p*-phenoxides

**Table 23.** Oxidation of sulfides to sulfoxides in acetone in the presence of copper complexes, 5–6 MPa<sup>220,221</sup>

| Sulfide          | Catalyst  | Catalyst concentration, mM | AcOH, M | T, °C | Reaction time, min | Yield of sulfoxide, mol. % |
|------------------|---|----------------------------|---------|-------|--------------------|----------------------------|
| Dimethyl sulfide | CuCl <sub>2</sub><br>(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> Cu  | 34                         | 3.3     | 130   | 5                  | 96                         |
|                  |   | 6.8                        | 0.2     | 140   | 10                 | 87                         |
|                  |   | 4.1                        | 0       | 140   | 20                 | 86                         |
|                  |   | 2.6                        | 0       | 150   | 20                 | 80                         |
|                  |   | 1.5                        | 0       | 150   | 25                 | 80                         |
|                  | (NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> Cu   | 4.9                        | 0       | 150   | 8                  | 94                         |
| Diethyl sulfide  | CuCl <sub>2</sub>   | 0.86                       | 0       | 140   | 20                 | 82                         |
|                  |   | 3                          | 0.01*   | 120   | 30                 | 100                        |
|                  | (C <sub>10</sub> H <sub>7</sub> O) <sub>2</sub> Cu<br>(NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> Cu | 8                          | 0.04*   | 130   | 30                 | 85                         |
|                  |   | 4                          | 0.17    | 140   | 30                 | 80                         |
|                  |   | 1.3                        | 0       | 150   | 20                 | 77                         |
| Dibutyl sulfide  | CuCl <sub>2</sub>   | 3                          | 3.3     | 120   | 10                 | 100                        |
| Thiolane         | CuCl <sub>2</sub>   | 3.9                        | 3.3     | 100   | 25                 | 95                         |
|                  |   | 3.9                        | 3.3     | 120   | 5                  | 90                         |
| 2-Ethylthiolane  | CuCl <sub>2</sub>   | 3.9                        | 3.3     | 100   | 10                 | 95                         |

\* trifluoroacetic acid.

**Table 24.** Oxidation of sulfides and sulfoxides to sulfones T = 150 °C, 5 MPa<sup>221,222</sup>

| Initial compound     | Catalyst, mM  |    | Acid, M   | Reaction time, min | Yield of sulfone, mol. % |
|----------------------|---|----|-----------|--------------------|--------------------------|
| Dimethyl sulfoxide   | CuCl <sub>2</sub>   | 13 | —         | 10                 | 85                       |
|                      | CuCl <sub>2</sub>   | 7  | AcOH, 3.3 | 15                 | 42                       |
|                      | CuBr <sub>2</sub>   | 34 | —         | 15                 | 91                       |
|                      | (NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> Cu | 33 | —         | 20                 | 100                      |
| Diethyl sulfide      | CuCl <sub>2</sub>   | 34 | AcOH      | 30                 | 100                      |
|                      | (NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> Cu | 32 | —         | 60                 | 100                      |
| Diethyl sulfoxide    | CuCl <sub>2</sub>   | 13 | —         | 10                 | 84                       |
|                      | CuBr <sub>2</sub>   | 34 | TFA*, 0.5 | 15                 | 91                       |
| Diisoamyl sulfide    | CuCl <sub>2</sub>   | 30 | AcOH, 3.3 | 10                 | 60**                     |
| Thiolane             | CuCl <sub>2</sub>   | 60 | AcOH, 3.3 | 20                 | 75                       |
|                      | CuCl <sub>2</sub>   | 34 | —         | 20                 | 60                       |
| Petroleum sulfides   | (NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> Cu | 30 | —         | 60                 | 60                       |
| Petroleum sulfoxides | CuBr <sub>2</sub>   | 34 | TFA, 0.5  | 20                 | 90                       |
|                      | (NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> Cu | 32 | TFA, 0.5  | 10                 | 63                       |

\* TFA — trifluoroacetic acid

\*\* T = 140 °C.

(RC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>Cu, naphthoxides (RC<sub>10</sub>H<sub>7</sub>O)<sub>2</sub>Cu, where R = H, NH<sub>2</sub>, CH<sub>3</sub>, OH (Tables 23 and 24).

The activities of copper compounds in the oxidation of diethyl sulfide to diethyl sulfoxide in acetone solution have been compared based on the rate constants of the first-order reaction (Table 25). As can be seen from Table 25, copper sulfate has the lowest activity, probably due to its solubility in acetone. The copper carboxylates which are dimeric in the initial state are one order of magnitude less active than the monomeric copper phenoxides. Pyrocatechol complexes of copper which are efficient in the oxidation of some compounds are inferior to copper phenoxides with respect to their activity towards the partial oxidation of diethyl sulfide.

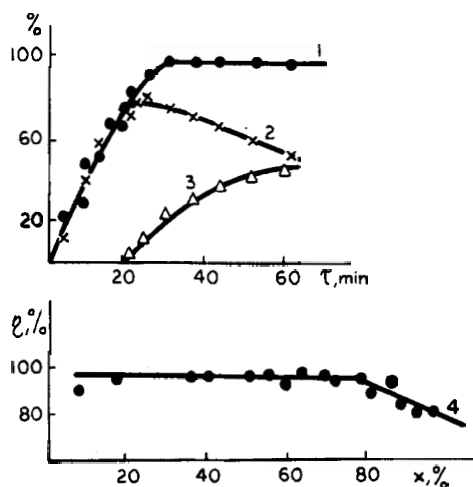
Among the Cu<sup>2+</sup> phenoxides, compounds with electron-donor substituents, i.e. *o*- and *p*-aminophenoxide and *p*-cresolate are the most active. It seems likely that in order for the copper phenoxide to exhibit a high activity in the oxidation of the sulfide the presence of a weak copper-ligand bond is necessary, since otherwise the access of the substrate to the coordination sphere is difficult.<sup>221</sup> Cu<sup>2+</sup> phenoxides in acetone solution do not decompose during the sulfide oxidation reaction. For example, in the oxidation of diethylsulfide (140 °C, 5 MPa) the yield of sulfoxide does not change even after 1000 mol of the product per g-ion of copper have been formed. The catalyst is little corrosive which allows its use in the production of such important product as sulfoxides and sulfones.

Dimethyl sulfide oxidation to dimethyl sulfoxide under air pressure in the presence of copper phenoxide catalysts has been further developed.<sup>224</sup> Based on kinetic and math-

**Table 25.** The activity of copper-containing catalysts in the oxidation of sulfides to sulfoxides at 140 °C, 5 MPa, and [AcOH] = 0.2 M<sup>221,222</sup>

| Compound                 | K, dm <sup>3</sup> /g-ion Cu·h<br>(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S | Petroleum sulfides |
|--------------------------|---|--------------------|
| Sulfate                  | 209   | 35                 |
| Acetate                  | 650   | 130                |
| Aminoacetate             | 90  | 30                 |
| Benzoate                 | 560   | 125                |
| Phthalate                | 437   | 116                |
| <i>o</i> -Aminophenoxide | 6000  | 800                |
| <i>p</i> -Aminophenoxide | 6240  | 820                |
| <i>p</i> -Cresolate      | 3000  | 400                |
| Phenoxide                | 1090  | 140                |
| 1-Naphthoxide            | 804   | 125                |
| Pyrocatecholate:         |   |                    |
| Cu:L = 1:1               | 147   | —                  |
| Cu:L = 1:2               | 722   | —                  |
| Chloride                 | 6600  | 900                |

emathical modeling data it is recommended to perform the reaction at conversions of dimethyl sulfide below 80 mol.% (100 wt.%). The recommended conditions are: 150 °C, 5 MPa, concentration of dimethyl sulfide in acetone 0.5 M, that of the catalyst 1.5 mM either in a piston flow reactor or in ideal mixing reactors placed in series. The selectivity towards the sulfoxide is close to 100% and the catalyst productivity is 1000 mol/g-ion

**Figure 17.** The influence of the reaction time on the conversion of diethyl sulfide (1), yield of diethyl sulfoxide (2), and of diethyl sulfone (3); the selectivity towards the sulfoxide at various conversion degrees of sulfide (4) over copper aminophenoxide, T = 140 °C, P = 6 MPa.<sup>221</sup>

$\text{Cu} \cdot \text{h}$ , which is higher by 2–3 orders of magnitude than the productivity achieved in the gas-phase oxidation of dimethyl sulfide.

The kinetics of the oxidation of various sulfides in acetone solution are the same for copper catalysts of different composition.<sup>207,209,220–224</sup> The conversion of the sulfide increases with increasing catalyst quantity and reaction time. The yield of the sulfoxide increases to a certain value and then falls because of its oxidation to the sulfone. The reaction rate increases proportionally with the concentration of the sulfide (first order with respect to sulfide) and does not change with the air pressure in the range 2.5 to 5 MPa (zeroth order with respect to oxygen) (Figure 17).

In acidic medium the reaction is facilitated, the rate being proportional to  $[\text{AcOH}]^{1/2}$ . The activation energy of the oxidation of dimethyl sulfide to the sulfoxide at 120–150 °C and 5 MPa and in the presence of a copper-phenoxide catalyst is  $71 \pm 4 \text{ kJ/mol}$ ;  $K_0 = 2675 \text{ h}^{-1}$ .

Regardless of the nature of the copper catalysts and the oxidation conditions the selectivity towards the sulfoxide is close to 100% at a sulfide conversion below 80%; at larger conversion further oxidation of the sulfoxide to the sulfone takes place:



The conversion of the sulfoxide to the sulfone in the presence of other homogeneous catalysts occurs similarly, but with a lower rate and selectivity than with copper catalysts with which a high yield of the sulfone can be achieved (Table 24). The extent of sulfoxide oxidation to sulfone increases with increasing temperature, contact time, and catalyst concentration. To attain a high yield of the sulfone more severe conditions are required, namely higher temperature, contact time, and sulfide conversion than for the oxidation of sulfides to sulfoxides.

The productivity with respect to the sulfones in the oxidation of individual and petroleum sulfides and sulfoxides reaches 250 ml/g-ion  $\text{Cu} \cdot \text{h}$ .

The interaction of a sulfide with a copper-containing catalyst leads to the formation of a complex.<sup>189,225</sup> As a result of sulfide coordination to  $\text{CuCl}_2$ , the bivalent copper is reduced, as follows from a decrease in the ESR signal assigned to  $\text{Cu}^{2+}$  with time in an argon atmosphere at 120 °C and 5 MPa (note also that a decolorization of the solutions is observed). The partial formation of a  $\text{Cu}^{2+} - \text{Cu}^+$  dimer bound via chloride ions has been deduced from the g-factors. It is, therefore, possible that the sulfide (like other donors<sup>226</sup>) can occupy an axial position in the complex with very weak activation. However, sulfide molecules enter mostly the equatorial plane of the complex by displacing water molecules from the coordination sphere of  $\text{Cu}^{2+}$ .

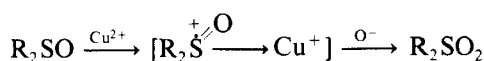
As shown by NMR studies<sup>189</sup> the complex formation of sulfides with copper acetylacetonate is accompanied by the incorporation of the sulfide in the axial plane of  $\text{Cu}^{2+}$  without noticeable electron density transfer from the sulfur atom to the copper ion. The complex is unstable and at room temperature dissociates completely. The interaction of  $\text{CuCl}_2$  with the sulfide leads to broadening and a downfield shift of the signals of  $\alpha$ -methylene groups in the  $^1\text{H}$  NMR spectrum and of the signals corresponding to  $\alpha$ - and  $\beta$ -carbon atoms in the  $^{13}\text{C}$  NMR spectrum. The high spin density of the protons of  $\text{CH}_3$  groups may be taken as evidence for the presence of a flat complex with equatorial sulfide ligands. In this situation an efficient interaction of a half-filled  $d_{x^2-y^2}$ -orbital of copper with the  $3p_z$ -orbital of sulfur takes place.  $\text{Cu}^{2+}$  serves as an electron acceptor and

the sulfide as an electron donor; 0.4 electrons being transferred from the sulfide to the copper ion. As a result, the effective charge of the copper is negative ( $-0.24$ ), i.e.  $\text{Cu}^{2+}$  is partially reduced. The complex is relatively unstable: the life-time of the sulfide molecule in the coordination sphere of  $\text{Cu}^{2+}$  is about  $10^{-10}$  s and the enthalpy of formation is 21 kJ/mol. As shown by quantum-chemical calculations, the complex formation leads to a redistribution of electron density and to the appearance of a positive charge on the sulfide sulfur atom; in other words, activation of the sulfide without C-S bond cleavage takes place. Probably, there appears a radical ion form  $[\text{R}_2\text{S}\cdots\text{Cu}^{2+}] \rightarrow [\text{R}_2\overset{+}{\text{S}}\cdots\text{Cu}^+]$ .

In the oxidative medium the radical cation can transform to a peroxide which reacts with the sulfide:



The sulfoxide can further be oxidized to the sulfone by a similar mechanism via formation of a donor-acceptor complex with the participation of the sulfur atom and  $\text{Cu}^{2+}$ :



Finally, the reduced copper ion is reoxidized by oxygen.

Thus, the high selectivity towards the products of partial oxidation of sulfides assisted by copper-containing complexes is caused by the involvement of a one-electron transfer without C-S bond cleavage.

It has also been suggested that the considerable acceleration of this process in acetone with an unchanged high selectivity towards the products of the partial oxidation of the sulfide might be due to participation of this solvent in the process, in particular, due to concomitant oxidation of acetone and sulfide. The oxidation of acetone occurs via  $\text{CH}_3\text{COCH}_2\cdot$  formation. This latter radical interacts with oxygen and thus transforms to a peroxide radical which should easily react with the sulfide and the sulfoxide to give their oxidation products.

In fact, under the conditions of sulfide oxidation acetone is partially (up to 1.5 mol.% at a 100% conversion) oxidized to acetic acid whose yield increases with increasing temperature, reaction time, and catalyst concentration.<sup>220,221</sup>

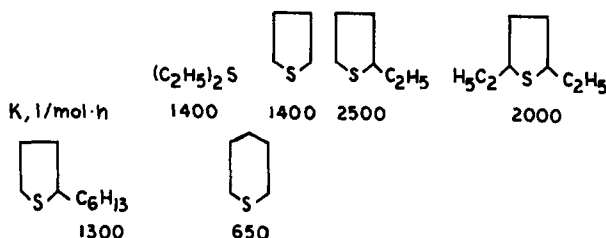
In the concomitant oxidation of sulfide and acetone the molar quantities of sulfide consumed and of acetic acid formed would be expected to be approximately the same. However, it has been found that the extent of acetone oxidation is independent of the sulfur compound, the reaction time, and the catalyst concentration. Under certain conditions the molar quantity of the sulfide consumed is higher by one order of magnitude than that of the acetic acid formed. The yield of the latter does not increase with increasing rate of the oxidation of the sulfide when its initial concentration is varied. In the presence of  $\text{MoS}_2$  (an acceptor of  $\text{RO}_2\cdot$  radicals) the extent of the oxidation of acetone decreases by a factor of 2.5, but the yield of the sulfoxide does not change. These data indicate that the high rate of the oxidation of the sulfide to the sulfoxide is not associated with the concomitant oxidation of acetone and a sulfur compound. The process is facile in acetone for the following reasons.

For the catalyst to show a high activity a fast recycling of  $\text{Cu}^{2+}$  ions is necessary.



Under the action of a sulfide  $\text{Cu}^{2+}$  can be reduced to give both  $\text{Cu}^+$  and  $\text{Cu}^0$  which is difficult to reoxidize with oxygen. In acetone as solvent the higher valent copper state is probably stabilized due to the formation of a polynuclear  $\text{Cu}^{2+}-\text{Cu}^+$  complex. The presence of  $\text{Cu}^{2+}$  necessary for sulfide activation and of  $\text{Cu}^+$  necessary for molecular oxygen activation in the cluster, as well as the complete homogenization of the system owing to the dissolution of the copper complex with sulfide and sulfoxide in acetone, provides a higher oxidation rate in acetone than in water, alcohol, or other solvents or in the absence of a solvent.<sup>223</sup>

Copper complexes in acetone exhibit group specificity, i.e. in their presence various sulfides can be oxidized. The rate of formation of the products of the partial oxidation of dialkyl sulfides<sup>222</sup> increases with increasing donor ability of the sulfur atom. Under comparable conditions at 100–150 °C and 5 MPa the rates of oxidation of dialkyl sulfides with  $\text{R} = \text{C}_1-\text{C}_5$  differ no more than by a factor of 2, which is due to closely similar donor abilities of the sulfur atoms in these compounds. The rate of oxidation of thiolane is close to that of diethyl sulfide with the same number of carbon atoms and nearly the same effective negative charge on the sulfur atom;<sup>194</sup> alkylthiolanes are oxidized more easily than thiacyclohexane. For example, in the presence of  $\text{CuCl}_2$  at 100 °C and 5 MPa the rate constants of the oxidation of sulfides to sulfoxides are:<sup>220</sup>



The oxidation of sulfides can also lead to the formation of sulfones. For example, at 150–200 °C, 5–8 MPa,  $[\text{CuCl}_2] = 60 \text{ mM}$ , and a reaction time of 20–60 min thiolane is oxidized to 80% thiolane 1,1-dioxide with 100% selectivity. Under more severe conditions the reaction is complicated by the formation of sulfonic acid.

The rate constant of oxidation of a sulfoxide to a sulfone is by a factor of 5–10 lower than the rate constant of oxidation of a sulfide to a sulfoxide. The oxidation of sulfoxides is difficult due to the poor donor ability of the sulfur atom in the sulfoxide and the coordination of part of the sulfoxide molecules to the catalyst via the oxygen atom of the SO group. Nonetheless, in the presence of copper complexes the rate of formation of sulfones is far higher than in the presence of other known catalytic systems.<sup>212,213</sup> An increase in the acidity of the reaction mixture leads to a decrease in the rate of the oxidation of sulfoxides to sulfones,<sup>222</sup> probably because of the formation of a stable  $\text{R}_2\text{SO}\cdots\text{H}$  complex which makes difficult the coordination of the sulfoxide to  $\text{Cu}^{2+}$  necessary for the occurrence of the oxidation reaction.

Unsaturated sulfides such as divinyl sulfide are difficult to oxidize on copper catalysts.<sup>222</sup> at 150 °C,  $[\text{Cu}^{2+}] = 64 \text{ mM}$ , and a reaction time of 30 min with a 0.15 M sodium trifluoroacetate additive the yield of sulfoxide is 20 mol.%. The reaction rate is lower by three orders of magnitude than that of the oxidation of saturated sulfides. This

fact is partly due to polymerization of divinyl sulfide (under the conditions mentioned above to an extent of 50%). The decrease of the reaction rate may be caused by a decrease in the electron density on the sulfur atom of divinyl sulfide due to conjugation of the electron pairs of the sulfur atom with the  $\pi$ -electron of the C=C bonds, and also due to partial coordination of divinyl sulfide to the catalyst via the C=C bonds (on the other hand, coordination via the sulfur atom is necessary for the formation of sulfoxide).

Copper catalysts can provide the oxidation of a natural mixture of sulfur-containing compounds by air,<sup>220,227</sup> e.g., of the so-called "oil sulfides" (a mixture of sulfur-containing compounds isolated from middle-distilled oil fractions deposited in the Siberian and Volga regions). The approximate composition of "oil sulfides" is as follows: thiamonocycloalkanes (40–60%), thiabicycloalkanes (10–20%), thiatricycloalkanes (4–8%), thiatetracycloalkanes (0–1.5%), thiaindanes (1.5–2.5%), cycloalkyl sulfides (2–4.5%), alkyl aryl sulfides (0–0.7%), dialkyl sulfides (2.5–9%). Under appropriate oxidation conditions sulfoxides and sulfones are formed.<sup>220,227</sup>

In the absence of a solvent  $\text{CuCl}_2$  is of low activity (the yield of sulfoxide is up to 50% and the productivity is up to 1 mol/g-ion Cu per h). The process is accompanied by the formation of large amounts of residues and resins. The activity of  $\text{CuCl}_2$  considerably increases in acetic acid; the sulfoxides formed contain side products and resin admixtures. A disadvantage of this catalytic system is the strong corrosivity of acetic acid. This disadvantage is eliminated when 2-propanol solution is used. A yield of sulfoxide of 70 mol.% with 80% selectivity can be achieved at 130 °C for 5 h, the productivity being ca. 4 mol/g-ion Cu·h. Regardless of the composition of the initial raw material the sulfoxides obtained contain side products such as sulfones, sulfonic acids, carbonyl compounds, and resins up to a total of 40–50%. Many of the above-mentioned shortcomings can be eliminated by the use of acetone as solvent.<sup>220,227</sup>

The oxidation of oil sulfides in acetone solutions occurs under the action of various copper compounds with high selectivity, the catalyst activity being dependent on its composition. The order of activity of the copper compounds studied towards formation of petroleum sulfoxides is the same as with individual sulfides (Table 25).

Under comparable conditions the oxidation of petroleum sulfides in acetone solution is by a factor of 5–10 slower than that of individual sulfides, but the rate of the sulfoxide formation is high, i.e. higher by two orders of magnitude than with other catalytic systems.

The selectivity towards sulfoxides, regardless of the nature of the catalyst, is close to 100% at a conversion of oil sulfides of up to 80 mol.%, but tends to decrease at larger conversions due to conversion of sulfoxides to sulfones, sulfonic acids, etc. The productivity is ca. 400 g of sulfoxides per 1 g of catalyst per h. Under appropriate conditions the oxidation of oil sulfides and sulfoxides yields sulfones (Table 24).

In hydrocarbon solutions in the presence of the  $\text{Cu}^{2+}$ -acetone system, sulfides are also oxidized to sulfoxides.<sup>220,223</sup>

At a constant content of hydrocarbons the kinetics of the oxidation are the same as in the absence of hydrocarbons (*vide supra*). At a content of up to 0.5–1 M of hydrocarbons in the reaction mixture the oxidation process is not inhibited. For example, the rate of the oxidation of hydrocarbon-free oil sulfides exceeds by no more than 10% (rel.) that of sulfides containing up to 20 wt.% of hydrocarbons. The oxidation of sulfides is dramatically (ca. by a factor of 10) suppressed upon addition of octane, cyclohexane, or

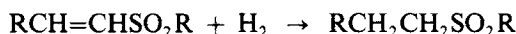
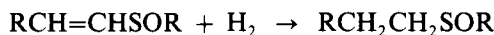
ethylbenzene in amounts of about 3 M. The rate of formation of individual and oil sulfoxides decreases proportionally with increasing concentration of hydrocarbons and increases with increasing concentration of sulfides.

This inhibition is caused by the competitive oxidation of the hydrocarbons in the presence of copper catalysts which leads to a decrease in the proportion of  $\text{Cu}^{2+}$  ions catalytically active in the oxidation of the sulfides. Under the conditions of sulfide oxidation hydrocarbons undergo conversions, aromatic hydrocarbons being oxidized more easily than naphthenes and paraffins. The oxidation leads to aldehydes, ketones, acids, and other oxygen-containing compounds. The addition of acceptors of  $\text{RO}_2$  radicals ( $\text{MoS}_2$ ) results in a decrease of the rate of hydrocarbon oxidations by more than one order of magnitude. Upon co-oxidation of hydrocarbons and sulfides the rate of conversion of hydrocarbons falls and the amount of the side-products formed decreases because the sulfides inhibit the oxidation of the hydrocarbons due to interaction with hydroperoxides.

Due to this fact sulfide-hydrocarbon mixtures and in particular oil sulfur compounds can be oxidized.<sup>220,227</sup>

### III.2. Catalytic Reduction of Unsaturated Sulfoxides and Sulfones by Hydrogen

A number of unsaturated sulfoxides and sulfones are readily available. In principle, their hydrogenation can provide the required corresponding saturated compounds. SO and  $\text{SO}_2$  groups activate multiple bonds of unsaturated sulfoxides and sulfones. Hence complex formation with a catalyst is possible and, if the catalyst can activate hydrogen, hydrogenation does take place:<sup>5</sup>



However, besides the saturation of  $\text{C}=\text{C}$  double bonds, there can take place some other processes and this complication is due to the specific properties of sulfur compounds.

The S–O bond in sulfoxides and sulfones is, at least partially, semipolar. Hence the electron density at the sulfur atom is decreased, which leads to a weakening of the C–S bonds. Since the sulfur atom is positively charged its ability for  $\text{pd}$ -conjugation rises, and hence the acidity also increases.

The oxygen atoms in sulfoxides and sulfones possess excess negative charge, due to which they are protonated and give addition products with the participation of an oxygen atom.

**III.2.1. Hydrogenation of sulfoxides** Sulfoxides easily coordinate with various metal compounds. The sulfur atom has a lone electron pair, hence complex formation with its participation is possible. The formation of such complexes has been confirmed in the case of the platinum group metals.<sup>2</sup> Sulfoxides coordinate with several metal compounds at the oxygen and sometimes they also coordinate at the sulfur. Thus, sulfoxides with their two donor atoms act as both thio and oxo ligands.<sup>2,228</sup> Due to this complex formation the sulfoxides are activated and become more reactive, in particular their decomposition is facilitated.<sup>2</sup> As a result of the complex formation of dimethyl sulfoxide with Rh(III) compounds, its reduction in solution to the sulfide proceeds more readily.<sup>229</sup>

On solid catalysts, e.g. on 5% Pd/C (17–25 wt.% relative to the sulfoxide), in ethanol solution at 80–90 °C, 3–9 MPa, and 1–4 days hydrogenation time, sulfoxides are hydrogenated to sulfides. The extent of the hydrogenation depends on the structure of the sulfoxides and reaches 80–99%.<sup>230</sup>

In unsaturated sulfoxides the SO group is more readily reduced than C=C bonds. For example, after three days of hydrogenation 66%  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{S}-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$  and 16%  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{S}-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$  were obtained from  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{SO}-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ . The yield of saturated sulfides also rises upon addition of activated carbon, but in this case no saturated sulfoxides were obtained.

*III.2.2. Hydrogenation of 2- and 3-thiolenes 1,1-dioxide* In solution, sulfones coordinate with various compounds, e.g., aluminum, titanium, tin, antimony, cobalt, and copper halides and Mn or Fe carbonyls.<sup>231,232,233</sup> Due to the complex formation of propylene sulfone with  $\text{Fe}_2(\text{CO})_9$ , the decomposition of the sulfone becomes easier.<sup>233</sup> It is thermodynamically probable that  $\text{SO}_2$  groups are reduced to sulfide. The patent literature<sup>234,235</sup> shows that at 250–400 °C on transition metal sulfides 2- and 3-thiolenes 1,1-dioxide and thiolane 1,1-dioxide are hydrogenated to thiolane. This reaction is complicated by concomitant dehydrogenation and decomposition. In the presence of molybdenum sulfide at 300–375 °C and 10 MPa dioctyl sulfone is reduced to a small extent to the sulfide, but mainly hydrogenolysis takes place to yield hydrocarbons.<sup>236</sup>

Unsaturated sulfones coordinate with rhodium, nickel, and platinum complexes<sup>237</sup> with the participation of their multiple bonds. Hence, addition of hydrogen to form unsaturated compounds becomes possible. A similar process also takes place with solid metal catalysts. The literature reports saturation of C=C double bonds of sulfones at 20 °C and 0.1 MPa in ethanol in the presence of unsupported or carbon-supported metallic palladium. Particularly, numerous data are available concerning the reduction of thiolene 1,1-dioxide in the presence of various catalysts.<sup>1,160,209,238–243</sup>

*III.2.2.1. Hydrogenation on metal complexes*  $\text{PdCl}_2$  complexes with dimethyl sulfide or dimethyl sulfoxide reduced with  $\text{KBH}_4$ - $\text{Pd}^\circ(\text{CH}_3)_2\text{S}$  and  $\text{Pd}^\circ(\text{CH}_3)_2\text{SO}$  in dimethyl sulfoxide solution catalyze the hydrogenation of 2- and 3-thiolenes 1,1-dioxide to thiolane 1,1-dioxide.<sup>244</sup>

The experiments were carried out in the kinetic region in a static volumetric shaken reactor system. At room temperature and 0.1 MPa the initial rate of thiolane dioxide formation is 1 mol/g-at. Pd·min. The Pd-DMF complex in *N,N*-dimethylformamide solution is approximately 45 times more active.

During the hydrogenation the above complexes are slowly deactivated due to interaction with  $\text{SO}_2$  formed by thiolene dioxide decomposition. The addition of bivalent sulfur compounds (thiophenes, thiolanes) to the reaction mixture decreases the activity of the complex. Thiophenes are stronger poisons than thiolanes. A 50% decrease in the initial activity of the complexes with sulfur ligands takes place after addition of 50–500 mmol/l of sulfur poisons to the solution. Palladium complexes with sulfur ligands are 10–100 times more stable to the thiolane effect than those with nitrogen-containing ligands. A conclusion about the reasons for the deactivation was made by UV and NMR studies of  $\text{Pd}^\circ(\text{CH}_3)_2\text{S}$  catalysts. The UV spectra of partially deactivated catalysts consisting of complexes treated with small quantities of thiolane exhibit bands typical for Pd(II)-

sulfur bonds ( $34\,000\text{--}24\,000\text{ cm}^{-1}$ ). At high thiolane concentrations (50 mmol/l and a ratio poison: Pd = 50) the spectra exhibit no such bands. The  $^{13}\text{C}$  NMR spectrum of the sample modified with thiolane exhibits signals belonging to thiolane coordinated with Pd ( $\delta$  40.3 and 32.8 ppm) and to free dimethyl sulfide ( $\delta$  20.6 ppm). This suggests that the deactivation is due to the displacement of the initial ligand from the coordination sphere of the complex by thiolane. This leads to the disintegration of the initial structure of the complex. In the presence of hydrogen metallic palladium is formed which is readily deactivated by sulfur compounds.

In 2-propanol solution  $\text{SiO}_2$ -supported mono- and polynuclear Pd(II) and  $\text{Pd}^0$  complexes (Table 20) at  $20^\circ\text{C}$  and 0.1 MPa catalyze the hydrogenation of 3-thiolene 1,1-dioxide; the yield of thiolane dioxide is 100% and the hydrogenation rate is  $1\text{--}90\text{ mol/g-at. Pd}\cdot\text{min.}^{158,159}$  The reaction on supported palladium complexes includes two main steps: the coordination of thiolene dioxide to form a complex, and hydrogen activation via the formation of a palladium hydride. The formation of the latter on Pd(II) complexes takes place when electron density is transferred from hydrogen to palladium whereas in the case of  $\text{Pd}^0$  complexes this transfer occurs in the reverse direction. This increase in the donor properties of the ligands increases the activity of the catalyst.<sup>245</sup>

During the hydrogenation of neat thiolene 1,1-dioxide all the complexes studied are stable, but upon prolonged operation of the process they are gradually deactivated under the effect of the bi- and tetravalent sulfur compounds formed during the process.<sup>158,159</sup>

**III.2.2.2. Hydrogenation on metal sulfides** Platinum group metal sulfides facilitate the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide at  $20^\circ\text{C}$  and 5 MPa, but are of low activity (Table 26). With increasing temperature the hydrogenation rate increases, but in this case the thiolene dioxide decomposes and the selectivity towards thiolane dioxide decreases.<sup>5,160,209</sup> For example, at  $100^\circ\text{C}$  and 5 MPa in the presence of 2.5% PdS/ $\text{Al}_2\text{O}_3$  catalyst in ethanol solution the yield of thiolane 1,1-dioxide after 2 h is 80% and the selectivity 90%.

Hydrogenation of 2-thiolene 1,1-dioxide on a platinum group metal and rhenium sulfide (1 g samples) at  $150^\circ\text{C}$  and 11 MPa in 2-propanol produces thiolane 1,1-dioxide in a yield of 50–100% with 70–90% selectivity. Ni, W, and Co sulfide are of low activity.

**Table 26.** Hydrogenation of 3-thiolene 1,1-dioxide in the presence of bulk catalysts at  $20^\circ\text{C}$  and 5 MPa<sup>160,209</sup>

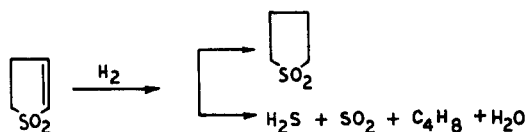
| Catalyst                | $v, \text{ g C}_4\text{H}_8\text{SO}_2/\text{g cat.}\cdot\text{h}$ |
|-------------------------|--|
| PdS                     | 4  |
| PdO                     | 10100  |
| Pd                      | 2560   |
| $\text{Rh}_2\text{S}_3$ | 7  |
| $\text{Rh}_2\text{O}_3$ | 0  |
| Rh                      | 8000   |
| $\text{PtS}_2$          | 2  |
| $\text{PtO}_2$          | 11000  |
| Pt                      | 316  |
| $\text{RuO}_2$          | 240  |
| Ru                      | 440  |

According to their specific activities ( $v \cdot 10^3 \text{ g/m}^2 \cdot \text{h}$ ) the catalysts examined can be arranged in the sequence:

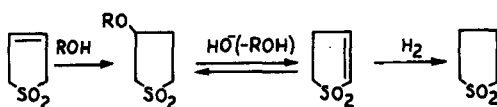
|                  |    |   |    |   |    |   |    |   |    |   |    |   |   |   |    |
|------------------|----|---|----|---|----|---|----|---|----|---|----|---|---|---|----|
| Sulfide of       | Rh | > | Re | > | Os | > | Pd | > | Pt | = | Co | > | W | > | Ni |
| $v_{\text{rel}}$ | 60 |   | 30 |   | 14 |   | 6  |   | 4  |   | 4  |   | 3 |   | 1  |

The catalysts which are the most active in the hydrogenation of 2-thiolene 1,1-dioxide are also the most selective towards the formation of thiolane 1,1-dioxide. These catalysts are stable during extended runs. For example, on 1 g PdS/Al<sub>2</sub>O<sub>3</sub> no less than 50 g of 2-thiolene 1,1-dioxide can be hydrogenated without loss of activity of this catalyst.<sup>246</sup>

Kinetic studies show that the reaction order with respect to hydrogen changes from first ( $P = 0.1\text{--}15 \text{ MPa}$ ) to zeroth ( $P > 15 \text{ MPa}$ ). The reaction is first order with respect to thiolene dioxide. Under certain conditions the hydrogenation is accompanied by hydrogenolysis of the starting material. These two reactions take place independently:



2-Thiolene 1,1-dioxide can be obtained from 3-alkoxythiolane 1,1-dioxides (sulfolanyl ethers) readily formed by interaction of alcohols with 3-thiolene 1,1-dioxide.<sup>247,248</sup> In alkaline media sulfolanyl ethers decompose to 2-thiolene dioxides which are reduced to thiolane 1,1-dioxides:

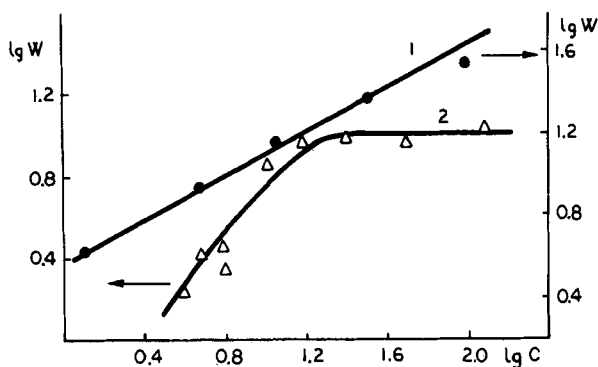


During the hydrogenation of sulfolanyl ethers ( $R = C_4\text{--}C_{12}$ ) in the presence of 2% PdS/Al<sub>2</sub>O<sub>3</sub> catalysts at 85–100 °C, 4–5 MPa, 0.25–2 h reaction time, and a ratio ether:alkali = 1:(0.2–5) the yield of thiolane 1,1-dioxide is 24–82 mol.% with a selectivity of 100%.

This reaction also takes place in the presence of metallic Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, but at a lower rate. At temperatures ranging within 20–85 °C and 0.1 MPa thiolane dioxides are obtained by hydrogenation of sulfolanyl ethers with  $R = C_4\text{--}C_{12}$  in alkaline solutions of alcohols, sulfolane, and water. A quantitative yield of thiolane dioxides is only obtained in aqueous alkaline solutions. The rate of hydrogenation is described by the following general equation:

$$v = K \cdot C_e \cdot P_{H_2} \cdot C_{KOH}^{1/2}$$

where  $C_e$  is the concentration of the sulfolanyl ether. At  $C_e > 0.1 \text{ mol/l}$  the reaction is zeroth order with respect to the ether. At  $C_e < 0.1 \text{ mol/l}$  it is first order (Figure 18) and



**Figure 18.** The logarithmic dependence of the rate of formation of thiolane 1,1-dioxide ( $v$ , mmol/lg cat · min) (0.5 g Pd/Al<sub>2</sub>O<sub>3</sub>,  $P = 0.1$  MPa) on KOH concentration ( $C \cdot 10^2$  mol/l) at  $T = 70^\circ\text{C}$ ,  $\tau = 30$  min,  $C_e = 0.08$  mol/l (1) and on the concentration of 2-butoxythiolane 1,1-dioxide ( $C \cdot 10^2$  mol/l) at  $T = 85^\circ\text{C}$ ,  $\tau = 20$  min and  $[\text{KOH}] = 0.89$  mol/l (2).<sup>248</sup>

the rate limiting step for the formation of the thiolane dioxide is the elimination of the alcohol from the ether rather than the reduction of the 2-thiolene dioxide formed.

For the first several minutes the reaction rate is maximal, but then it sharply drops because of catalyst deactivation. This deactivation cannot be prevented by hydrogenation on one catalyst sample and batchwise introduction of the substrate into the reaction medium in amounts ensuring a constant ether concentration. At 70–85 °C and a KOH concentration of 0.45–0.9 mol/l the amount of thiolane dioxide formed per 1 g catalyst prior to the tenfold drop in the initial reaction rate, is independent of the ether concentration in the initial solution and equals 0.45–0.67 g. The deactivation of the catalyst is assumed to be caused by the decomposition products of thiolene 1,1-dioxide formed from the sulfolanyl ethers which are produced in alkaline medium.

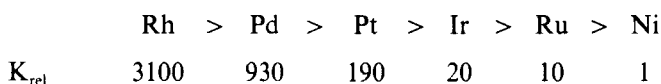
**III.2.2.3. Hydrogenation on metals** At room temperature palladium, platinum, and ruthenium oxide are highly active in the hydrogenation of 3-thiolene 1,1-dioxides while rhodium oxide is inactive (Table 26). This is determined by the effect of the metals formed by reduction of the oxides. Pd, Pt, and Ru oxide are easily reduced to metals. Their activity per unit surface is identical with the specific activity for the metal blacks of these metals. For example, the specific activity ( $K \cdot 10^3$  g/m<sup>2</sup> metal · h) for Pd, PdO, Pt, PtO<sub>2</sub>, Ru, and RuO<sub>2</sub> is 11, 8, 2.3, 2.2, 0.12, and 0.06, respectively. Rhodium oxide is first reduced to the metal at higher temperatures, hence it is inactive in the formation of thiolane 1,1-dioxides.

Group VIII metals are usually applied as catalysts for the low-temperature hydrogenation of various unsaturated organic compounds. Their activity is ascribed to the inability to form donor (“dative”) bonds with C=C groups, which leads to the activation of these bonds. This possibility also exists for unsaturated compounds such as 2- and 3-thiolene 1,1-dioxide where the C=C bond is activated by an SO<sub>2</sub> group.

Under the effect of group VIII metals the hydrogenation of 2- and 3-thiolene oxide readily takes place already at room temperature with 100% selectivity towards thiolane 1,1-dioxide (Table 26). The rate per 1 g catalyst is 100–1000 times higher than that on metal sulfides.<sup>5,209</sup>

It is thermodynamically possible to reduce sulfonyl groups to sulfide ones, but on metals this reaction does not take place. The reason is that, for this reaction to occur, the  $\text{SO}_2$  group must be activated by complex formation with charge transfer from the oxygen to a metal atom, which requires the metal to possess vacant low-energy orbitals. Apparently, this process takes place during the interaction of the sulfone with metal compounds.

The laws for the selection of metal catalysts to reduce thiolene dioxides are the same as those for alkenes. For example, according to their specific activities group VIII metals (metal blacks and supported catalysts) during the kinetic hydrogenation of 3-thiolene dioxides (20 °C, 5 MPa, sulfolane and 2-propanol) follow the same sequence as in the hydrogenation of other unsaturated compounds



**Table 27.** Dispersity and activity of palladium catalysts<sup>249-252</sup>

| Support                        | Pd concentration<br>(wt. %) | $\left(\frac{\mu\text{mol}}{\text{m}^2 \text{cat.}}\right)$ | Surface area<br>$\left(\frac{\text{m}^2}{\text{g Pd}}\right)$ | Activity,*<br>weight<br>$\left(\frac{\text{g}}{\text{g}\cdot\text{h}}\right)$ | $\text{K}\cdot 10^{-3}$<br>specific<br>$\left(\frac{\text{g}}{\text{m}^2 \text{Pd}\cdot\text{h}}\right)$ |
|--------------------------------|-----------------------------|---|---|---|--|
| $\gamma\text{-Al}_2\text{O}_3$ | 0.5                         | 27  | 260   | 10  | 8  |
|                                | 1.0                         | 51  | 220   | 18  | 8  |
|                                | 1.8                         | 100   | 180   | 30  | 9  |
|                                | 2.0                         | 83  | 210   | 40  | 10   |
|                                | 2.0                         | 168   | 110   | 26  | 12   |
|                                | 2.0                         | 250   | 80  | 16  | 10   |
|                                | 2.7                         | 147   | 140   | 45  | 12   |
|                                | 4.5                         | 250   | 110   | 60  | 12   |
|                                | 6.3                         | 346   | 70  | 60  | 14   |
|                                | 9.6                         | 505   | 50  | 62  | 13   |
|                                | 13.5                        | 794   | 45  | 75  | 12   |
| AlSi                           | 18.0                        | 1200  | 38  | 90  | 13   |
|                                | 0.5                         | 14  | 314   | 12  | 8  |
|                                | 1.0                         | 28  | 280   | 16  | 6  |
|                                | 2.0                         | 56  | 200   | 24  | 6  |
|                                | 3.0                         | 84  | 130   | 30  | 8  |
|                                | 5.0                         | 140   | 110   | 40  | 5  |
| Activated carbon               | 1.0                         | 10  | 195   | 13  | 6  |
|                                | 2.0                         | 20  | 165   | 25  | 8  |
|                                | 3.0                         | 30  | 190   | 34  | 3  |
|                                | 5.0                         | 50  | 170   | 42  | 5  |
| $\text{SiO}_2$                 | 0.5                         | 17  | 100   | 3   | 6  |
|                                | 1.0                         | 33  | 80  | 5   | 7  |
|                                | 2.0                         | 67  | 60  | 8   | 7  |
|                                | 3.0                         | 100   | 45  | 10  | 7  |
|                                | 5.0                         | 167   | 30  | 15  | 10   |
|                                | 8.0                         | 267   | 30  | 20  | 8  |

\* the activity was determined at 20 °C, 5 MPa, C = 5 wt.%, and a weight ratio of catalyst to  $\text{C}_4\text{H}_6\text{SO}_2$  of 1:200.



One can observe that the catalytic activity of metals depends on the properties of their d-electron shells.

The hydrogenation rate of 3-thiolen dioxide per catalyst weight ("weight" activity) rises with increasing metal surface area (degree of metal dispersity). The dispersity was determined by several independent methods: X-ray analysis, electron microscopy, chemisorption of oxygen, carbon oxide, and sulfur dioxide, and by following the poisoning of the catalyst by sulfur poisons during hydrogenation. These different methods give very similar values for the dispersity.<sup>249-252</sup> As a rule, the surface area of the metals decreases with increasing concentration in the samples (Tables 27 and 28). The metal dispersity depends on its surface concentration irrespective of whether the support surface or its metal content is varied. The dependence of the metal dispersity on the surface concentration is linear over a considerable range. The data obtained for a given metal supported by various substrates do not fall on one straight line due to differences in the crystallization behavior of the metal due to e.g., the different strength of the metal-support bonds and the associated different surface mobility. The most drastic decrease of the dispersity with increasing surface concentration of palladium is observed on SiO<sub>2</sub> and the least decrease on Al<sub>2</sub>O<sub>3</sub> and AlSi. On carbon the dispersity of palladium does not change at all in the concentration range examined. On Al<sub>2</sub>O<sub>3</sub>, AlSi, and carbon the dispersity of palladium is highest. A low dispersity of palladium is achieved when it is supported on zeolites or on substrates with small surface area such as corundum or carborundum. Similar relationships are also observed with rhodium.

The metal dispersity also depends on how the metal is supported on the substrate. Palladium modification with boron increases the surface area of the former, e.g. the surface areas of palladium black and of Pd + 3% B are 8 and 18 m<sup>2</sup>/g, respectively. The X-ray spectrograms of these samples are identical, i.e. in the presence of boron only the dispersity of the palladium increases, but the phase composition does not change. A similar observation was also made for Pd samples modified with silver.<sup>251</sup> The surface areas of palladium catalysts grow when palladium is modified with ruthenium, rhodium, platinum, or iridium (Table 29). According to the X-ray data for samples reduced at

**Table 28.** Dispersity and activity of supported rhodium<sup>249-252</sup>

| Support                        | Rh concentration |   | Surface area                                  | Activity, weight  | K · 10 <sup>-3</sup> * specific                                     |
|--------------------------------|------------------|---|---|---|---|
|                                | (wt. %)          | $\left(\frac{\mu\text{mol}}{\text{m}^2 \text{cat.}}\right)$ | $\left(\frac{\text{m}^2}{\text{g Rh}}\right)$ | $\left(\frac{\text{g}}{\text{g} \cdot \text{h}}\right)$ | $\left(\frac{\text{g}}{\text{m}^2 \text{Rh} \cdot \text{h}}\right)$ |
| Al <sub>2</sub> O <sub>3</sub> | 0.5              | 30  | 415   | 30  | 14  |
|                                | 1.0              | 47  | 350   | 68  | 19  |
|                                | 2.0              | 125   | 320   | 110   | 17  |
|                                | 3.0              | 170   | 240   | 100   | 14  |
|                                | 5.0              | 312   | 245   | 200   | 16  |
|                                | 10.0             | 570   | 205   | 385   | 19  |
| SiO <sub>2</sub>               | 2.0              | 78  | 130   | 29  | 17  |
|                                | 3.0              | 116   | 105   | 42  | 19  |
|                                | 5.0              | 195   | 83  | 60  | 21  |

\* refer to the note in Table 27.

**Table 29.** The activity and stability of alloys in the hydrogenation of 3-thiolen 1,1-dioxide at 20°C<sup>253</sup>

| Catalyst | Promoting additive to Pd (wt.%) | S, (m <sup>2</sup> /g) | K · 10 <sup>-3</sup> * (g/g·h) | Yield of C <sub>4</sub> H <sub>8</sub> SO <sub>2</sub> ** (g/g) |
|----------|---------------------------------|------------------------|--------------------------------|---|
| Pd       | 0                               | 5                      | 69                             | 160   |
| Pd-Pt    | 5                               | 18                     | 305                            | 180   |
|          | 10                              | 13                     | 273                            | 190   |
|          | 15                              | 24                     | 471                            | 200   |
|          | 35                              | 30                     | 580                            | 200   |
|          | 50                              | 37                     | 552                            | —   |
|          | 75                              | 81                     | 507                            | 200   |
|          | 100                             | 88                     | 276                            | —   |
| Pd-Ir    | 5                               | 37                     | 416                            | 200   |
|          | 10                              | 43                     | 392                            | 200   |
|          | 25                              | 51                     | 49                             | —   |
|          | 100                             | 162                    | 1                              | —   |
| Pd-Rh    | 10                              | 45                     | 363                            | 350   |
|          | 25                              | 74                     | 386                            | 600   |
|          | 50                              | 104                    | 606                            | 800   |
|          | 70                              | 103                    | 168                            | 200   |
|          | 80                              | 96                     | 21                             | —   |
|          | 90                              | 91                     | 13                             | —   |
| Rh       | 100                             | 162                    | 0                              | 200   |
| Pd-Ru    | 10                              | 17                     | 174                            | 220   |
|          | 25                              | 58                     | 337                            | 300   |
|          | 50                              | 78                     | 232                            | —   |
|          | 70                              | 89                     | 206                            | —   |
|          | 80                              | 130                    | 92                             | 60  |
| Ru       | 100                             | 114                    | 6                              | 30  |

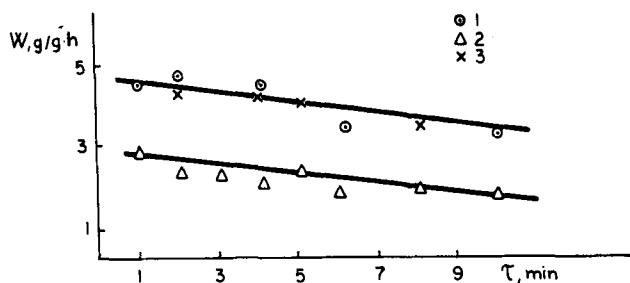
\* K = rate constant of the first order in magnitude.

\*\* yield of product per 1 g catalyst prior to its complete deactivation.

20°C, in all cases solid solutions are formed, except in the case of Pd-Rh of the composition 1:1 which is a mechanical mixture of these metals.<sup>253</sup>

The weight activity of catalysts in the hydrogenation of 3-thiolen 1,1-dioxide increases with increasing metal content, which is associated with the increasing total surface area of the metal in the catalyst. By varying the support type and the method of supporting the metal and by introducing promoting additives it is possible to change the metal dispersity and hence to affect its weight activity (Tables 27 and 28).

For palladium catalysts promoted by platinum metals the maximal weight activities are observed to be dependent on the composition (Table 29). According to certain concepts, the maximal catalytic activity of alloys should be reached when the number of electron vacancies in the d-layer per one metal atom is equal to unity. It has been found, however, that Pd-Pt catalysts also give maximum activities although both metals have the same number of vacancies.<sup>253</sup> When Pd is modified by promoting additives, the energy of the hydrogen bond to the surface changes. For example, during the hydrogenation of thiolen dioxide the potentials of Pd and Pd-Pt catalysts shifts towards the anode region by approximately 130 and 90 mV, respectively. In the latter case this



**Figure 19.** Hydrogenation of 3-thiolen 1,1-dioxide at  $T = 20^{\circ}\text{C}$ ,  $P = 0.1\text{ MPa}$  over 2%  $\text{Pd}/\text{Al}_2\text{O}_3$  in its oxidized (1) and reduced (2) form, 3 — regenerated catalyst heated *in vacuo* at  $300^{\circ}\text{C}$ .<sup>254</sup>

indicates a certain strengthening of the hydrogen bond to the surface. This also affects the activity of the catalyst.

In short-term (0.5–1.0 min) determinations of the activity of mixed oxides there is only time for  $\text{PdO}$  to be reduced to the metal. The less readily reducible rhodium, ruthenium, and iridium oxide cannot be reduced and hence the active component of palladium catalysts is the metal. The total surface area of the samples increases when  $\text{PdO}$  is modified with Rh, Ru, Ir, and Pt. Hence it can be suggested that the palladium dispersity increases in their presence.<sup>253</sup> The weight activity of palladium and rhodium increases<sup>254</sup> if the hydrogen-reduced catalyst is treated with air at  $50\text{--}250^{\circ}\text{C}$  for 2 h (Figure 19). The specific sulfur capacity of the metals in samples reduced with hydrogen at  $300^{\circ}\text{C}$  is lower than in those treated with air at  $200^{\circ}\text{C}$ . This indicates an increase in the number of active sites on the catalyst after its activation with air. In this case the metals can be assumed to form the corresponding oxides. For the activity of palladium catalysts this is not essential since  $\text{PdO}$  is readily reduced to the metal already at room temperature. Therefore hydrogen species strongly bonded to Pd cannot form. Rhodium oxide is hardly reduced to the metal, therefore it is inactive. The X-ray data of samples oxidized with air for different periods of time show that palladium black samples oxidized at  $100\text{--}400^{\circ}\text{C}$  for 10 h only exhibit lines typical of metallic palladium. The lines of  $\text{PdO}$  appear only after treatment of Pd with air at  $500^{\circ}\text{C}$ . Similar observations were also made with rhodium samples. Thus, treatment of Pd and Rh in air at  $T \leq 300\text{--}400^{\circ}\text{C}$  does not lead to the formation of bulk oxides.

The observed increased activity of Pd and Rh catalysts after treatment with air is caused by the elimination of hydrogen strongly bonded to the surface. The weight activity of these catalysts reduced with hydrogen at  $300^{\circ}\text{C}$  increases if they are heated *in vacuo* at  $300^{\circ}\text{C}$  for 20 h.<sup>254</sup>

The activity of metal catalysts can also be increased without changing the dispersity of the metal. For example, if Raney nickel is promoted with vanadium, molybdenum, zirconium, or niobium, this does not affect the nickel dispersity, but increases by 2–7 times its weight activity due to changes in the composition of the active component of the catalyst.<sup>255</sup>

Irrespective of the metal content and the support type, the specific activity of catalysts for the hydrogenation of thiolene dioxides (the activity per metal surface area) is constant within 20 rel. % (the size of crystallites varying by up to  $20\text{ \AA}$ )<sup>5,209</sup> (Tables 27 and 28).

**Table 30.** Hydrogenation of 3-thiolene 1,1-dioxide on nickel-chromium catalysts<sup>253</sup>

| Catalyst                            | Pt additive to NiCr, wt. % | $K \cdot 10^{-3} *$<br>g/g · h | Yield of $C_4H_8SO_2 *$<br>g/g |
|-------------------------------------|----------------------------|--------------------------------|--------------------------------|
| NiCr <sub>2</sub> O <sub>3</sub>    | 0                          | 4.2                            | 18                             |
| Ni-Cr <sub>2</sub> O <sub>3</sub> - | 0.2                        | 2.1                            | 23                             |
| Pt                                  | 0.6                        | 3.6                            | 25                             |
|                                     | 1.0                        | 4.2                            | 31                             |
|                                     | 2.0                        | 3.7                            | 41                             |
|                                     | 4.0                        | 4.1                            | 50                             |
| Pt-Cr <sub>2</sub> O <sub>3</sub>   | 1.0                        | 0.1                            | 0.2                            |

\* refer to the notes in Table 29.

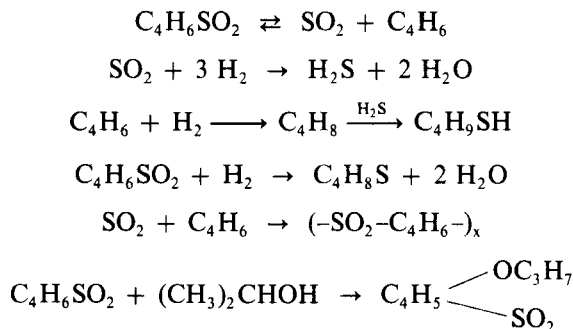
Metals are sufficiently stable during the hydrogenation of 3-thiolene 1,1-dioxide since the sulfur atom is screened and the formation of sulfur-metal bonds is hindered. However, during long-lasting hydrogenation the activity of the catalyst decreases. One of the reasons for this decrease can be the removal of hydrogen from the surface, since it is known that some metals, e.g. palladium and nickel, can dissolve large quantities of hydrogen.<sup>152</sup> The extent of the removal of hydrogen from the surface can be estimated from the change of the potential of the catalysts during the hydrogenation. The potential of nickel catalysts (20 °C, 0.1 MPa, in 2-propanol solution, neutral medium) shifts towards the anode region by 250–300 mV. This is due to strong adsorption of thiolene dioxide and to the displacement of most of the hydrogen from the surface. When the hydrogenation is interrupted the potential is lower than before the reaction, which could be due to the partial removal of hydrogen from the surface. A similar effect has also been observed for ruthenium whose potential shifts towards the anode region by about 600 mV.

When nickel is promoted with other metals the extent of hydrogen removal by thiolene dioxide from the surface of the catalyst can decrease. For example, upon modification of nickel-chromium catalysts with platinum the potential shift towards the anode region upon addition of thiolene dioxide is 100 mV, whereas on unpromoted catalysts it is 300 mV. The initial activity of the catalyst remains unchanged, but the stability of Pt-NiCr is approximately three times higher than that of NiCr (Table 30).<sup>253</sup>

The increased stability cannot be ascribed to additional hydrogenation on the metal promoters. Apparently, upon addition of Pt to NiCr, the degree of hydrogen removal from the surface during the hydrogenation decreases with the strengthening of the hydrogen-surface bond. Surface hydrogen can inhibit the interaction between catalysts and poisons contained in the raw material. With strengthening hydrogen-surface bonds the dissociative adsorption of thiolene dioxide to form contact poisons is hindered. Modification of Raney nickel catalysts with Mo, V, Zr, or Nb increases their stability in the hydrogenation of 3-thiolene 1,1-dioxide 2–7 times due to the changes in the composition of their active components.<sup>255</sup> This, however, cannot completely eliminate the metal deactivation during thiolene dioxide hydrogenation, since it is largely due to surface blocking by poisons formed during the hydrogenation. Owing to the ability of the oxygen atoms of the SO<sub>2</sub> group to form bonds with metals or metal carriers it is

possible that weak C-S bonds will be weakened and dissociate. The sulfone molecules can also dissociate due to the formation of the  $d_{\pi}-d_{\pi}$  bond  $M \leftarrow :S \leftarrow$  and the easy loss of  $\alpha$ -hydrogen atoms from the sulfones.<sup>5</sup>

This reaction of 3-thiolenes 1,1-dioxide is exothermic by 113 kJ/mol). With incomplete removal of heat local overheating can occur, due to which both in the bulk of the catalyst and on its surface the thermal dissociation of thiolenes dioxide and the formation of contact poisons take place. It is possible that the following reactions take place:



One of the main primary products of thiolenes dioxide decomposition, i.e. 1,3-butadiene, exerts practically no effect on the activity of the catalyst in the hydrogenation of unsaturated sulfones. Water, polysulfones, and sulfolanyl ethers can deactivate catalysts to some extent. The deactivation of the catalyst largely takes place under the effect of sulfur-containing decomposition products of thiolenes dioxide, i.e.  $SO_2$ ,  $H_2S$ ,  $RSH$ , and  $C_4H_8S$ .

It is most likely that the main deactivating agent for metals during the hydrogenation of thiolenes dioxide is  $SO_2$ . This can be deduced from the following facts.<sup>153</sup>

3-Thiolenes 1,1-dioxide is thermally unstable and upon storage even at room temperature it partly decomposes to form  $SO_2$ . The decomposition rate increases with increasing temperature. The stability of catalysts, e.g. of  $Pd/Al_2O_3$  decreases by a factor of 2.5 when the temperature rises from 20 to 50 °C. Modification of the hydrogenated solution with  $SO_2$  leads to catalyst deactivation. The amount of  $SO_2$  necessary for complete deactivation of palladium catalysts and their sulfur capacity with respect to  $SO_2$  are approximately equal. The rates of metal deactivation and adsorption are obey a linear relationship. Treatment of the catalyst at 20 °C with gaseous  $SO_2$  prior to the experiments leads to its deactivation. Approximately, a decrease of its initial activity by a factor of 20 is observed. Deactivated catalysts contain Pd sulfate which is inactive in the hydrogenation of thiolenes dioxide. The stability of the metals increases with decreasing  $SO_2$  content of the initial solution. For example, when the  $SO_2$  concentration in the solution falls from 0.0015 to 0.0002 wt.%, a five-fold increase in catalyst stability is observed. Upon adding bases or peroxide-alkali mixtures to the hydrogenated solution  $SO_2$  is removed, but the activity of the catalyst still diminishes due to a change in its properties.

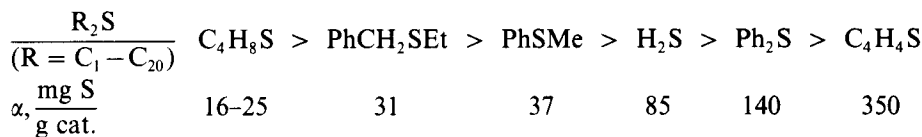
$SO_2$  chemisorption on metals produces surface complexes of the composition 1:1 without disruption of the initial structure.  $SO_2$  is a strong  $\pi$ -acceptor affecting the donor ability of metals which activates C=C bonds in sulfones. The ability of the metal to activate hydrogen can be preserved, but the activity of the catalyst decreases. With

**Table 31.** The activity and stability of group VIII metals during the hydrogenation of 3-thiolene 1,1-dioxide at 20 °C and 5 MPa<sup>153</sup>

| Metal     | Activity,<br>$\frac{\text{mol C}_4\text{H}_8\text{SO}_2}{\text{h} \cdot \text{m}^2 \text{ metal}}$ | Yield of<br>$\text{C}_4\text{H}_8\text{SO}_2$ ,<br>$\frac{\text{mmol}}{\text{m}^2 \text{ metal}}$ | Time elapsed<br>until complete<br>metal deac-<br>tivation,<br>min |
|-----------|--|---|---|
| Rhodium   | 311  | 230   | 3   |
| Palladium | 93   | 85  | 4   |
| Ruthenium | 19   | 20  | 5   |
| Iridium   | 2  | 7   | 6   |
| Platinum  | 1  | 4   | 8   |
| Nickel    | 0.1  | 3   | 35  |

respect to their stability to the poisoning effect of added SO<sub>2</sub>, metals follow the same sequence as during extended hydrogenation of pure 3-thiolene 1,1-dioxide, which points to a common reason for the deactivation of the catalyst. The less active a metal is the more resistant is it. The amount of thiolane 1,1-dioxide obtained per 1 m<sup>2</sup> accessible metal before the complete disappearance of the initial activity increases with increasing catalyst activity (Table 31). It is associated with the same amount of SO<sub>2</sub> admixture in the initial solution and the close rate of substrate decomposition on various metals. Sulfur dioxide forms more stable complexes with nickel, ruthenium, and rhodium than with palladium. SO<sub>2</sub> adsorption on Pd is reversible and when the catalyst is washed with water or acetone or heated in a nitrogen atmosphere, SO<sub>2</sub> is removed from its surface and the catalyst regenerated.

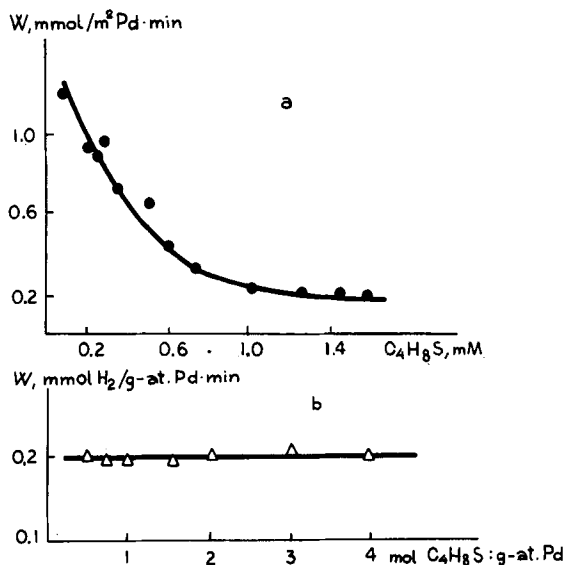
The SO<sub>2</sub> formed during the hydrogenation of 3-thiolene 1,1-dioxide is partially reduced to H<sub>2</sub>S which is also a strong poison for metals. When H<sub>2</sub>S interacts with metals dissociative irreversible chemisorption takes place to produce a surface metal sulfide which prevent the activation of hydrogen. Catalyst deactivation is the direct consequence of the formation of donor-acceptor complexes  $\text{M} \leftarrow \text{SH}_2$ . With regard to their toxicity in the hydrogenation of 3-thiolene 1,1-dioxide poisons follow the sequence showing corresponding to changes in the electron-donor properties of the sulfur in these compounds:



For sulfides a linear dependence between Taft's inductive constants and the toxicities has been established,<sup>5</sup> which is indicative of the formation of metal-sulfur bonds under the deactivation. According to the literature<sup>256,257</sup> metals, in particular Pd, can essentially be protected against deactivation by sulfur compounds by their support on acid zeolites or activated carbon. To elucidate this possibility a proper estimate of a catalyst's

stability during hydrogenation is necessary. Published estimates concerning the sensitivity of metals to the effect of poisons are conflicting. In order to compare the sulfur resistance of catalysts the hydrogenation of sulfur-containing materials is often carried out<sup>153</sup> under standard conditions. The catalyst stability is determined from the product yield or the total conversion obtained after a certain reaction time, sometimes corresponding to the attainment of stable hydrogenation. This estimate for the sulfur stability cannot be considered to be correct. It is especially inappropriate for the comparison of catalysts with different metal dispersions, since the degree of hydrogenation changes proportionally to the surface area of the active components. Nowadays a generally accepted characteristic for the catalyst activity is the reaction rate, measured in the kinetic region, per unit surface of the active component. To determine the relative stability of catalysts it is necessary to consider changes in their specific activity under the effect of poisons.

Most often the deactivation of catalysts takes place largely due to a decrease of the number of active centers because of poison chemisorption. At constant temperature the adsorption rate and the amount of a substance adsorbed per unit weight or on the catalyst surface depend only on the poison concentration in the reaction mixture. Hence it is necessary to consider changes in the specific activity of the catalysts depending on the poison concentration in the reaction mixture rather than on the poison/catalyst ratio (cf. e.g. Figure 20). If the reaction is carried out on different catalysts and if the surface area does not change with time, in order to obtain an approximate estimate for the sulfur stability it is possible to consider instead of the change in the specific activity of catalysts the conversion degree of the initial substrate or the product yield. It is necessary,



**Figure 20.** The specific rate of 3-thiolene 1,1-dioxide hydrogenation (1% Pd/Al<sub>2</sub>O<sub>3</sub>, 20°C) vs. thiolane concentration in solution: (a) mol C<sub>4</sub>H<sub>8</sub>S:g-at. Pd = 1; (b) 0.5 mmol/l concentration of thiolane.<sup>258</sup>

**Table 32.** The activity and sulfur-stability of palladium catalysts<sup>258</sup>

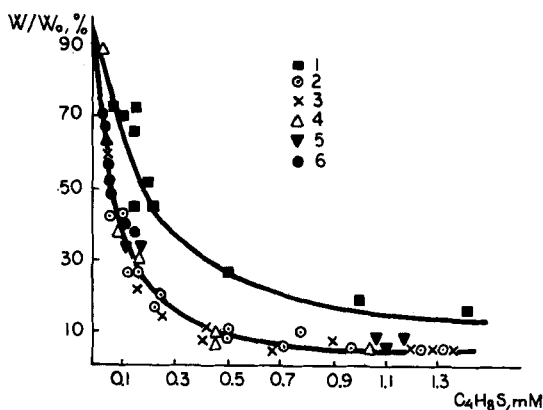
| Support                        | Pd,<br>wt. % | S,<br>$\frac{\text{m}^2}{\text{g Pd}}$ | Hydrogenation rate<br>of pure $\text{C}_4\text{H}_6\text{SO}_2$ |  | Poison<br>$\frac{\text{mmol}}{\text{l}}$ | v/v, % upon adding<br>$\text{C}_4\text{H}_8\text{S}$ $\text{C}_4\text{H}_4\text{S}$ |    |
|--------------------------------|--------------|--|---|--|--|---|----|
|                                |              |  | $\frac{\text{mol H}_2}{\text{g-at. Pd} \cdot \text{min}}$       | $\frac{\text{mol H}_2}{\text{m}^2 \text{Pd} \cdot \text{min}}$<br>$10^4$ |  |   |    |
| $\gamma\text{-Al}_2\text{O}_3$ | 0.1          | 380                                    | 174   | 49   | 0.24                                     | 14  | 22 |
|                                | 1.0          | 260                                    | 102   | 42   | 0.24                                     | 18  | 24 |
|                                | 0.5          | 300                                    | 147   | 52   | 0.78                                     | 8   | 12 |
|                                | 1.0          | 260                                    | 102   | 42   | 0.78                                     | 5   | 12 |
|                                | 1.0          | 260                                    | 102   | 42   | 0.05                                     | 53  | 46 |
|                                | 1.0          | 260                                    | 102   | 42   | 0.1                                      | 36  | 27 |
|                                | 1.0          | 260                                    | 102   | 42   | 0.15                                     | 27  | 26 |
|                                | 1.0          | 260                                    | 102   | 42   | 0.5                                      | 9   | 22 |
| $\text{SiO}_2$                 | 0.1          | 220                                    | 46  | 22   | 0.24                                     | 14  | —  |
|                                | 1.0          | 67                                     | 16  | 26   | 0.24                                     | 12  | 21 |
|                                | 0.5          | 130                                    | 42  | 34   | 1.2                                      | 4   | 7  |
|                                | 1.0          | 67                                     | 16  | 26   | 1.2                                      | 4   | —  |
| AlSi<br>amorphous              | 0.2          | 140                                    | 37  | 28   | 0.45                                     | 5   | 22 |
|                                | 1.0          | 75                                     | 22  | 31   | 0.45                                     | 8   | —  |
|                                | 0.5          | 65                                     | 23  | 37   | 1.2                                      | 4   | 10 |
|                                | 1.0          | 75                                     | 22  | 31   | 1.2                                      | 3   | 19 |
| Activated<br>carbon            | 1.0          | 165                                    | 58  | 37   | 0.5                                      | 8   | 21 |
|                                | 5.0          | 84                                     | 24  | 31   | 1.2                                      | 5   | 9  |
| NaY zeo-<br>lites:             |              |  |   |  |  |   |    |
| 7.8% Na                        | 1.0          | —                                      | 5   | —  | 0.15                                     | 66  | —  |
| 1.5% Na                        | 1.0          | —                                      | 4   | —  | 0.15                                     | 64  | —  |
| 0.9% Na                        | 1.0          | —                                      | 5   | —  | 0.15                                     | 57  | 72 |
| 0.9% Na                        | 1.0          | —                                      | 5   | —  | 1.0                                      | 19  | 17 |
| Pd black                       | 100          | 40                                     | 10  | 25   | 0.1                                      | 42  | —  |
|                                | 100          | 40                                     | 10  | 25   | 0.24                                     | 20  | —  |

however, that the conversion degree is below 100% and that no diffusional obstacles are present.

To establish the role of supports in the stability of a metal to the toxic effect of bivalent sulfur compounds, palladium catalysts have been examined in the liquid-phase hydrogenation of 3-thiolene 1,1-dioxide.<sup>258</sup> For all catalysts a decrease in the activity was observed in the presence of thiolene and thiolane. The most drastic changes in the deactivation rate were observed with a poison concentration of as much as 0.1–0.2 mmol/l, where the deactivation rate decreases. With poison concentrations above 2–3 mmol/l the catalysts are practically completely deactivated (Table 32, Figure 21).

The toxicity of thiophenes and thiolane is of the same order of magnitude. The stability values determined from the ratio of reaction rates with and without poisons ( $v/v_0$ ) for the catalysts 1% Pd supported on  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , carbon, and aluminosilicate are practically the same and coincide with the data obtained for palladium black. A 50% drop in the activity of these catalysts is obtained with about 0.06 mmol/l thiolane. Palladium support on carbon did not lead to any increase in the sulfur stability compared to  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and aluminosilicate catalysts. At the same concentration of poisons in the solution  $v/v_0$  changes only slightly with varying palladium content on this support.





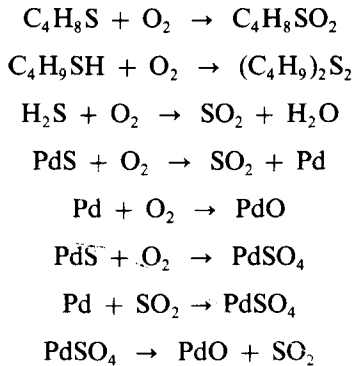
**Figure 21.** The catalyst stability in the hydrogenation of 3-thiolene 1,1-dioxide vs. thiolane concentration in solution: 1 — 1% Pd/NaY: ■ — 7.8, □ — 1.5 and ▣ — 0.9% Na; 2 — Pd supported on  $Al_2O_3$ ,  $SiO_2$ , C, AlSi, and Pd black.<sup>258</sup>

Since the surface areas of Pd in the samples differ approximately by an order of magnitude, it can be assumed that for the catalysts examined changes in the Pd dispersity exert practically no effect on the stability of the catalyst to deactivation by bivalent sulfur compounds. In low-temperature liquid-phase hydrogenation the metal dispersity changes only slightly. Under the effect of reaction media mainly the number of accessible metal atoms decreases since sulfur poisons are chemisorbed on metals. The metal surface area in the initial and deactivated samples is the same. Hence for a quantitative estimate of catalyst sulfur stability it is possible to consider changes in the hydrogenation rate per unit weight of the catalyst or per 1 g-at. metal.

Experiments with the hydrogenation of thiolene dioxide on palladium-zeolite catalysts showed that these are of low activity. With poison concentrations as high as 2 mmol/l the  $v/v_0$  value is approximately twice as high as in the case of palladium supported on the other substrates. This is ascribed to a decrease of poison concentration in the solution, since zeolites, being good adsorbents of sulfur compounds, absorb thiolane to a greater extent than the other substrates examined. But zeolite substrates do not provide complete protection for palladium against its deactivation and already with 2.5 mmol/l thiolane the residual activity  $v/v_0$  is only 2.7%. The Pd-zeolite catalysts examined differ in their acidity but no relationship between the catalyst stability and its sodium content is found. Hence changes in the electron configuration of palladium under the effect of acid centers of the zeolite lattice are not responsible for the stability of Pd to the toxic action of sulfur compounds. Thus, the sulfur resistance of these catalysts does not depend on the Pd dispersity on different types of supports.

Ni, Ru, and Rh metal deactivated by sulfur compounds cannot be regenerated, neither in inert nor in oxidizing media, by rinsing with various solvents and oxidants, or by reduction with hydrogen. Raney nickel after repeated leaching does not completely regain its initial activity. The regeneration of these catalysts is impeded by the high stability of their surface sulfur compounds. Palladium compounds possess a relatively low thermal stability, hence such catalysts deactivated during the hydrogenation of thiolene dioxide can be regenerated. Pd catalysts can be regenerated by treatment with

hydrogen at elevated temperatures. But a more effective method of regeneration<sup>259</sup> is that based on the treatment of deactivated catalysts with air at 50–300 °C under conditions desorption of surface-bonded sulfur compounds and chemical conversion of surface sulfides and sulfates as well as mild oxidation of sulfur poisons to form nontoxic compounds take place:



As noted above, the reduction of Pd oxide to the metal takes place readily at room temperature. Hence, after regeneration of the catalyst with air further treatment with hydrogen at elevated temperatures is not required.

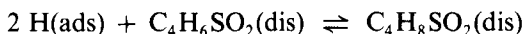
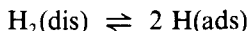
Kinetic studies of the liquid-phase hydrogenation of 3-thiolen 1,1-dioxide have been performed<sup>106,239–243</sup> in the presence of various metal catalysts with 2-propanol, thiolane 1,1-dioxide, or mixtures of these as solvent. The kinetic region for the hydrogenation in a static system is relatively easily reached when the process is carried out on catalyst grains smaller than 0.1 mm. At 0.1 MPa hydrogen pressure the reaction is first order with respect to hydrogen and zeroth order with respect to thiolen dioxide. Here the reaction takes place under conditions where the concentration of thiolen dioxide is much higher than that of hydrogen, due to the low solubility of the latter in the solvent. Besides, thiolen dioxide removes a considerable amount of hydrogen from the catalyst surface (the shift of the catalyst potential towards the anode region upon introducing a substrate into the solution is 130–600 mV). The catalyst surface appears to be saturated with the hydrogenated product, hence the reaction rate does not depend on its concentration. Hydrogen has almost no access to the surface and under these conditions the reaction rate is limited by the hydrogen activation.

A pressure increase above 1–2 MPa increases the hydrogen concentration in the solution and facilitates its access to the contact surface of metals. This leads to a change in the ratio of reactants on the surface and hence to a change in the reaction mechanism. Adsorption rates of 3-thiolen 1,1-dioxide on metals are higher than the reaction rate, hence its adsorption cannot be the limiting step of the process. The surface coverage by the substrate is sufficiently high. These facts suggest that the hydrogenation takes place in areas of high surface coverage and proceeds via the activation of hydrogen on the surface and its interaction with dissolved thiolen dioxide.

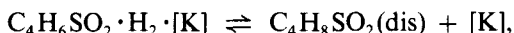
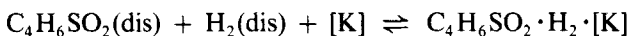
Since the adsorption rate of thiolen dioxide is high, its concentration on the surface can be treated as being in equilibrium with the liquid phase.

At pressures above 1–2 MPa the reaction rate is independent of the partial pressure of hydrogen and increases, up to a certain limit, with the concentration of 3-thiolen

1,1-dioxide beyond which the rate no longer depends on the substrate concentration. Taking into account the kinetic schemes for the liquid-phase hydrogenation examined by S. L. Kiperman,<sup>260</sup> one can assume that at high pressures and average concentrations of 3-thiolene 1,1-dioxide (the reaction is zeroth order with respect to hydrogen and first order with respect to thiolene dioxide) the rate limiting step of the reaction is the interaction of hydrogen predominantly adsorbed on the surface with thiolene dioxide activated by its contact with a metal:



The overall zeroth order with respect to both reactants at high concentrations of thiolene dioxide in the solution and high pressures of hydrogen can be interpreted if the hydrogenation is assumed to follow the scheme



where [K] is the catalyst. An active complex is formed with the participation of hydrogen, thiolene dioxide, and the catalyst. This process takes place at a high rate and then slow decomposition of this complex yields thiolane 1,1-dioxide.

For preparative purposes thiolane 1,1-dioxide is synthesized in two steps. 3-Thiolene 1,1-dioxide is obtained from 1,3-butadiene and  $\text{SO}_2$  without catalyst and then hydrogenated in a liquid phase in the presence of nickel or palladium catalysts. Palladium catalysts are two–three orders of magnitude more active than nickel catalysts. The useful operation time of alumo-palladium catalysts until the conversion degree decreases from 100 to 98% is no less than 600 h and the yield of thiolane 1,1-dioxide as high as 100 g/g catalyst. Deactivated catalysts can be regenerated by heating in air.

## REFERENCES

1. A. V. Mashkina, *Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Khimiya, Moscow, 1964), Vol. 6, pp. 146–192.
2. D. Martin and H. G. Hauthal, *Dimethylsulfoxid* (Akademie-Verlag, Berlin, 1971), 494 p.
3. N. K. Lyapina, *The Chemistry and Physical Chemistry of Sulfur-Organic Oil Distillates* (Nauka, Moscow, 1984).
4. E. N. Karaulova, *Usp. Khim.* **57**, 1131 (1988).
5. A. Mashkina, *Catalytic Synthesis and Conversion of Heterocyclic Compounds* (Zinatne, Riga, 1976), pp. 31–52.
6. H. O. Folkins and E. L. Miller, *Ind. Eng. Chem., Process Design Develop.* **1**, 271 (1962); *C.A.* **57**, 13215 (1962).
7. O. Weisser, *Chem. Prum.* **17**, 307 (1967).
8. O. Weisser and S. Landa, *Sulphide Catalysts, Their Properties and Applications* (Czechoslovak Academy of Sciences, Prague, 1972), p. 278.
9. H. O. Folkins and E. L. Miller, *Proc. Am. Petr. Inst. Sect. III* **42**, 188 (1962).
10. V. E. Mazaev and M. A. Korshunov, *Catalysts for the Production and Conversion of Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 7–21.
11. M. F. Pankratova and Yu. M. Pinegina, *Kinet. Katal.* **12**, 390 (1971).
12. M. M. Miki, T. Ito and B. Kimura, *J. Soc. Org. Synth. Chem., Tokyo* **24**, 471, 482 (1966).
13. A. V. Mashkina, E. A. Paukshtis, E. N. Yurchenko, V. N. Yakovleva and A. V. Popov, *React. Kinet. Catal. Lett.* **34**, 407 (1987).

14. A. V. Mashkina, R. I. Maksimovskaya, V. N. Yakovleva and E. P. Starodubtseva, *React. Kinet. Catal. Lett.* **36**, 159 (1988).
15. A. V. Mashkina, E. A. Paukshtis and V. N. Yakovleva, *Kinet. Katal.* **29**, 596 (1988).
16. A. V. Mashkina, E. A. Paukshtis and V. N. Yakovleva, *Kinet. Katal.* **29**, 1174 (1988).
17. A. V. Mashkina, E. A. Paukshtis and V. N. Yakovleva, *Kinet. Katal.* **30**, 1239 (1989).
18. M. Ziolk and J. Bresinska, *Zeolites* **5**, 245 (1985).
19. M. Ziolk, J. Bresinska and H. G. Zarge, *Acta Phys. Chem.* **31**, 551 (1985); *C.A.* **104**, 19316 (1986).
20. M. Ziolk, D. Szuba and R. Leksowski, *Innovation in Zeolite Materials Science* (Elsevier, Amsterdam etc., 1988), pp. 427–434.
21. A. V. Mashkina and V. N. Yakovleva, *React. Kinet. Catal. Lett.* **44**, (1991) (in press).
22. V. B. Kazanskii, *Usp. Khim.* **57**, 1937 (1988).
23. A. A. Davydov, *IR Spectroscopy in the Chemistry of Surface Oxides* (Nauka, Novosibirsk, 1984), p. 219.
24. G. Busca, P. F. Rossi, V. Lorenzelli, H. Benaissa, J. Travert and J.-C. Lavalley, *J. Phys. Chem.* **89**, 5433 (1985).
25. J. Novakova, L. Kubelkova and Z. Dolejsk, *J. Catal.* **108**, 208 (1987).
26. J. D. Gay, *J. Phys. Chem.* **84**, 3230 (1980).
27. P. Salvador and M. L. G. Gonzalez, *J. Colloid. Interface Sci.* **56**, 577 (1976).
28. M. L. Unland, *J. Phys. Chem.* **82**, 580 (1978).
29. K. N. Zhdanova, O. V. Ishchenko, Yu. B. Yan, N. V. Alekseeva and F. K. Shmidt, *Zh. Fiz. Khim.* **61**, 1529 (1987).
30. C. D. Chang, *Catal. Rev.* **25**, 2 (1983).
31. G. Busca, P. Forzatti, J. C. Lavalley and E. Franconi, *Catalysis by Acids and Bases* (Elsevier, Amsterdam etc., 1985), Vol. 20, pp. 15–24.
32. V. I. Yakerson, L. I. Lafer, V. Ya. Danyushevskii and A. M. Rubinshtein, *Izv. Akad. Nauk SSSR. Ser. Khim.* **10**, 2247 (1967).
33. L. I. Vladyko, Yu. M. Garmashev and A. I. Trokhimets, *Kinet. Katal.* **25**, 884 (1984).
34. V. M. Mastikhin, I. L. Mudrakovsky, A. V. Nosov and A. V. Mashkina, *J. Chem. Soc., Faraday Trans. 1*, **85** 2819 (1989).
35. R. W. Glass and R. A. Ross, *J. Phys. Chem.* **77**, 2571 (1973).
36. C. Meyer and J. Bastick, *Bull. Soc. Chim. Fr.*, 59 (1974).
37. Y. Okamoto, M. Oh-Hara, A. Maezawa, T. Imanaka and S. Teranishi, *J. Phys. Chem.* **90**, 2396 (1986).
38. J. V. Desyatov, E. A. Paukshtis and A. V. Mashkina, *React. Kinet. Catal. Lett.* **41**, 161 (1990).
39. K. Aomura, *Kenkyu Hobun—Asahikawa Kogyo Koto Senmon Gakko* **25**, 1 (1988); *C.A.* **109**, 40408 (1988).
40. A. M. Deane, D. L. Griffiths, J. A. Lewis, J. A. Winter and A. J. Tench, *J. Chem. Soc., Faraday Trans. 1*, 1005 (1975).
41. H. G. Karge and J. Raska, *J. Colloid. Interface Sci.* **64**, 522 (1978).
42. W. J. Jones and R. A. Ross, *J. Chem. Soc. (A)*, 1787 (1968).
43. M. Demertzis, D. Kovaleva-Demertzis and E. F. Vansant, *Bull. Soc. Chim. Belg.* **35**, 145 (1986).
44. I. V. Desyatov, E. A. Paukshtis and A. V. Mashkina, *React. Kinet. Catal. Lett.* **41**, 85 (1990).
45. T. L. Slager and C. H. Amberg, *Canad. J. Chem.* **50**, 3416 (1972).
46. F. E. Massoth, *J. Catal.* **36**, 164 (1975).
47. Y. M. Dadiza and J. M. Saleh, *J. Chem. Soc., Faraday Trans. 1*, 1678 (1973).
48. H. G. Karge, M. Laniecki and M. Ziolk, *J. Catal.* **109**, 252 (1988).
49. H. G. Karge, M. Ziolk and M. Laniecki, *Zeolites* **7**, 197 (1987).
50. O. Saur, T. Chevreau, J. Lamotte, J. Travert and J.-C. Lavalley, *J. Chem. Soc., Faraday Trans. 1*, 427 (1981).
51. A. Datta and G. Cavell, *J. Phys. Chem.* **89**, 450 (1985).
52. A. V. Deo, J. G. Lana and U. W. Habgood, *J. Catal.* **21**, 270 (1971).
53. C. Meyer and J. Bastick, *Bull. Soc. Chim. Fr.*, 463 (1979).
54. H. Saussey, J. C. Lavalley, M. Ziolk and J. Kujawa, *Heterogeneous Catalysis (6th Int. Symp., Part 1, Sofia, 13–18 July, 1987)*, pp. 462–467.
55. H. Saussey, O. Saur and J. C. Lavalley, *J. Chim. Phys. Phys.-Chim. Biol.* **81**, 261 (1984).
56. R. W. Glass and R. A. Ross, *J. Phys. Chem.* **77**, 2576 (1973).
57. E. M. Davydova, Yu. M. Shchekochikhin and A. V. Mashkina, *Kinet. Katal.* **11**, 1514 (1970).
58. E. M. Davydova and Yu. M. Shchekochikhin, *Kinet. Katal.* **15**, 1550 (1974).
59. A. V. Mashkina, *Organic Sulfur Compounds* (Zinatne, Riga, 1980), Vol. 2, pp. 432–444.
60. J. Ferino, R. Monaci, E. Rombi and V. Solinas, *Thermochim. Acta* **135**, 371 (1988).

61. V. M. Mastikhin, I. L. Mudrakovskii and S. V. Filimonova, *Chem. Phys. Lett.* **149**, 175 (1988).
62. J. Datka and Z. Piwowarska, *Zeolites* **8**, 30 (1988).
63. W. Przystajko, R. Fiedorov and J. G. Dalla Lana, *Zeolites* **7**, 477 (1987).
64. A. N. Gorshkova, L. V. Strukova, V. N. Vinogradova, L. P. Batasheva and F. A. Milman, *Kinet. Katal.* **27**, 526 (1986).
65. J. Barrault, M. Guisnet, J. Lucien and R. Maurel, *Bull. Soc. Chim. Fr.*, 362 (1977).
66. Z. A. Nabutovskii and A. M. Tsybulevskii, *Neftekhimiya* **27**, 114 (1987).
67. M. Ziolk, J. Kujawa and P. Decyk, *Zeolites* **8**, 54 (1988).
68. I. L. Knunyants and A. V. Fokin, *Usp. Khim.* **19**, 545 (1950).
69. E. N. Prilezhaeva and M. F. Shostakovskii, *Usp. Khim.* **32**, 897 (1963).
70. S. Oae, *The Chemistry of Organic Sulfur Compounds* (Khimiya, Moscow, 1975), p. 78.
71. Y. B. Kazanskii, *5th International Symp. on the Relation between Homogeneous and Heterogeneous Catalysis* (Institute of Catalysis, Novosibirsk, 1986), Vol. 1, pp. 87–106.
72. M. Sugioka and K. Aomura, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, 471 (1973).
73. M. Sugioka and K. Aomura, *Bull. Jpn. Petrol. Inst.* **18**, 14 (1976).
74. M. Sugioka and K. Aomura, *Bull. Jpn. Petrol. Inst.* **17**, 51 (1975).
75. T. Kamanaka, M. Sugioka and K. Aomura, *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1156 (1976).
76. M. Sugioka, T. Kamanaka and K. Aomura, *J. Catal.* **52**, 531 (1978).
77. N. V. Shelemina, T. A. Danilova and B. V. Ramanovskii, *Neftekhimiya*, 295 (1969).
78. Y. K. Al-Haidary and J. M. Saleh, *J. Chem. Soc., Faraday Trans. 1*, 3027, 3043 (1988).
79. A. V. Mashkina, V. R. Grunvald, V. I. Nasteka, B. P. Borodin, V. N. Yakovleva and L. N. Khairulina, *React. Kinet. Catal. Lett.* **41**, 357 (1990).
80. M. Sugioka, I. Hirono and K. Aomura, *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1597 (1972).
81. M. Sugioka and K. Aomura, *Bull. Jpn. Petrol. Inst.* **15**, 136 (1973).
82. K. Aomura, *Kenkyu Hobun—Asahikawa Kogyo Senmon Gakko* **25**, 11 (1988); *C.A.* **109**, 40409 (1988).
83. M. Sugioka and K. Aomura, *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1279 (1973).
84. M. Sugioka and K. Aomura, *Int. Chem. Eng.* **13**, 755 (1973).
85. M. Sugioka and K. Aomura, *Bull. Fac. Eng. Hokkaido Univ.*, 195 (1974); *C.A.* **81**, 90866 (1974).
86. M. Sugioka and K. Aomura, *Bull. Fac. Eng. Hokkaido Univ.*, 207 (1974); *C.A.* **81**, 90867 (1974).
87. T. Kamanaka, M. Sugioka and K. Aomura, *Bull. Jpn. Petrol. Inst.* **19**, 41 (1977).
88. M. Sugioka and K. Aomura, *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1153 (1978).
89. M. Sugioka and K. Aomura, *Bull. Fac. Eng. Hokkaido Univ.*, 135 (1978), *C.A.* **91**, 38481 (1979).
90. I. V. Kozhevnikov, S. Ts. Khakhasaeva and S. M. Kulikov, *Kinet. Katal.* **29**, 76 (1988).
91. S. N. Koshelev, A. V. Mashkina and N. G. Kalinina, *React. Kinet. Catal. Lett.* **39**, 367 (1989).
92. R. D. Obolentsev and L. N. Gabdullina, *The Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Akademiya Nauk SSSR, Moscow, 1959), Vol. 2, pp. 183–199.
93. M. Sugioka and K. Aomura, *Bull. Fac. Eng. Hokkaido Univ.*, 187 (1974); *C.A.* **81**, 90865 (1974).
94. V. Yu. Zakharov, B. V. Romanovskii and O. M. Zakharov, *Catalysts for the Production and Conversion of Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 30–32.
95. T. S. Sukhareva, L. V. Shepel and A. V. Mashkina, *Kinet. Katal.* **19**, 654 (1978).
96. R. D. Obolentsev and L. N. Gabdullina, *The Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Gostoptekhizdat, Moscow, 1961), Vol. 4, pp. 145–150.
97. R. D. Obolentsev and L. N. Gabdullina, *The Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Khimiya, Moscow, 1964), Vol. 6, pp. 324–330.
98. R. Obolentsev and L. N. Gabdullina, *The Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Bashkir Department, Akademiya Nauk SSSR, Ufa, 1960), Vol. 3, pp. 261–270.
99. Kh. I. Areshidze and M. K. Gadzhiev, *Catalytic Conversions of Sulfur-Organic Compounds Supported on Alumosilicates* (Metsniereba, Tbilisi, 1974).
100. Kh. I. Areshidze, M. K. Gadzhiev and N. M. Nebieridze, *Neftekhimiya* **16**, 476 (1976).
101. S. N. Koshelev, N. G. Kalinina, V. A. Poluboyarov, V. F. Anufrienko and A. V. Mashkina, *Kinet. Katal.* **30**, 679 (1989).
102. N. G. Kalinina, V. A. Poluboyarov, V. F. Anufrienko, S. N. Koshelev, A. V. Mashkina and V. S. Danilovich, *Kinet. Katal.* **28**, 1253 (1987).
103. E. M. Davydova, Yu. M. Shchekochikhin and A. V. Mashkina, *Kinet. Katal.* **17**, 459 (1976).
104. S. N. Koshelev, E. A. Paukshtis, N. A. Verkhoturova and A. V. Mashkina, *Kinet. Katal.* **29**, 376 (1988).
105. A. V. Mashkina, *Kinet. Katal.* **12**, 116 (1971).
106. A. V. Mashkina, *Heterogeneous Catalysis in the Production and Conversion of Heterocyclic Compounds* (Zinatne, Riga, 1971), pp. 203–220.
107. H. C. van der Plas, *Ring Transformations of Heterocycles* (Academic Press, London–New York,

- 1973), 484 p.
108. Yu. K. Yur'ev, *Catalysis in High School* (Moscow State University, Moscow, 1962), Part 2, Vol. 1, pp. 176-185.
109. Yu. K. Yur'ev and M. D. Prokina, *Zh. Obshch. Khim.* **7**, 1868 (1937).
110. Yu. K. Yur'ev, *Zh. Obshch. Khim.* **21**, 742 (1951).
111. J. Hirao and H. Hatta, *J. Pharm. Soc. Jpn.* **74**, 446 (1954).
112. B. Loev and J. T. Massengale (Pennsalt Chemicals Corp.), U.S. **2,899,444** (1959); *C.A.* **54**, 572 (1960).
113. L. Hodossy, E. Haidegger and D. Kriza (Peti Nitrogenmuvek), *Fr.* **1,596,273** (1970); *C.A.* **74**, 125404 (1971).
114. E. Worbs, G. Meyer and H. Mägerlein (Glanzstoff A.-G.), *Ger. Offen.* **1,936,565** (1971); *C.A.* **74**, 111909 (1971).
115. T.E. Deger, B. Buchholz and R. H. Goshorn (Pennsalt Chemicals Corp.), *Brit.* **913,584** (1962); *C.A.* **59**, 2776 (1963).
116. Y. Ono, T. Mori and K. Hatada, *Acta Phys. Chem.* **24**, 233 (1978); *C.A.* **89**, 179173 (1978).
117. Tuong Van Dao, A. A. Kubasov and K. V. Topchieva, *Vestnik Mosk. Univ., Khim.* **14**, 146 (1973); *C.A.* **79**, 52540 (1973).
118. I. V. Desyatov, V. N. Yakovleva and A. V. Mashkina, *React. Kinet. Catal. Lett.* **41**, 97 (1990).
119. A. V. Mashkina, *Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds, All-Union Symp., Abstr.* (Institute of Organic Synthesis, Riga, 1987), pp. 13-15.
120. G. Odian, *Principles of Polymerization* (McGraw-Hill Book Co., New York, 1970).
121. J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides* (John Wiley & Sons, New York etc., 1963).
122. T. S. Petukhova, A. A. Fateeva, E. I. Dobkina, V. M. Komarov and E. V. Kolesova, *Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds, All-Union Symp., Abstr.* (Institute of Organic Synthesis, Riga, 1987), pp. 172-173.
123. A. A. Fateeva, V. M. Komarov, I. M. Golubkov, Yu. S. Koltsov, Yu. E. Malkov and E. V. Kolesova, *Catalytic Processes and Catalysts* (Leningrad Technological Institute, Leningrad, 1987), p. 119.
124. S. Tonomura, S. Yanamatsu and A. Aoshima, *8th Japan-USSR Catalysis Seminar* (Tokyo, 1986), pp. 29-31.
125. H. Meerwein, D. Delfs and H. Morschel, *Angew. Chem.* **72**, 927 (1960).
126. S. Tonomura, S. Yanamatsu and A. Aoshima (Asahi Chem. Ind. Co.), *Jpn.* **61,143,428** (1986); *C.A.* **105**, 191818 (1986).
127. A. V. Mashkina, T. S. Sukhareva and V. I. Chernov, *Neftekhimiya* **7**, 301 (1967).
128. E. N. Guryanova, I. P. Goldshtein and I. P. Romm, *Donor-Acceptor Bonds* (Khimiya, Moscow, 1973).
129. G. S. Denisov, L. A. Kuzina and A. Ya. Smolyanskii, *Zh. Obshch. Khim.* **57**, 196 (1987).
130. K. Fujita, K. Hatada, Y. Ono and T. Keii, *J. Catal.* **35**, 325 (1974).
131. Y. Ono, K. Hatada, K. Fujita, A. Halgeri and T. Keii, *J. Catal.* **41**, 322 (1976).
132. I. V. Ivakina, *Zh. Obshch. Khim.* **57**, 1600 (1987).
133. E. B. Ludvig, B. A. Rosenberg, T. M. Zvereva, A. R. Gantmakher and S. S. Medvedev, *Vysomolek. Soedin.* **7**, 269 (1965).
134. E. Furimsky, *Ind. Eng. Chem. Prod. Res. Develop.* **22**, 3134 (1983).
135. F. M. Latypova, Yu. I. Lyakhovetskii, N. K. Lyapina and Z. N. Parnes, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 597 (1985).
136. D. N. Kursanov, Z. N. Parnes, M. I. Kalinkin and N. M. Loim, *Ionic Hydrogenation* (Khimiya, Moscow, 1979), p. 61.
137. G. K. Borezkov, *Heterogeneous Catalysis* (Nauka, Moscow, 1986).
138. S. G. Gagarin, A. P. Kovtun, A. A. Krichko and V. P. Sachenko, *Kinet. Katal.* **20**, 1138 (1979).
139. R. D. Obolentsev and A. V. Mashkina, *Hydrogenolysis of Sulfur-Organic Compounds of Oils* (Gostoptekhizdat, Moscow, 1961).
140. J. Kraus and M. Zdravil, *React. Kinet. Catal. Lett.* **6**, 475 (1977).
141. E. J. Markel, G. L. Schrader, N. N. Sauer and R. J. Angelici, *J. Catal.* **116**, 11 (1989).
142. B. Radomyski, J. Szczygiet and J. Trawczynski, *Appl. Catal.* **25**, 295 (1986).
143. R. Golding, E. Molnar, O. Abrams and Z. Katan, *Rev. Port. Quim.* **19**, 203 (1977); *C.A.* **93**, 26190 (1980).
144. N. P. Davidova and P. Kovacheva, *Neftekhimiya* **22**, 93 (1982).
145. T. P. Voskresenskaya and T. S. Sukhareva, *React. Kinet. Catal. Lett.* **36**, 307 (1988).
146. T. P. Voskresenskaya, T. S. Sukhareva and L. V. Manuilova, *Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds, All-Union Symp., Abstr.* (Institute of Organic Synthesis, Riga, 1989), pp. 135-136.

147. A. A. Zirka, *Synthesis and Reactivity of Organic Sulfur Compounds*, 17th All-Union Conf., Abstr. (Tbilisi, 1989), p. 265.
148. A. A. Zirka and A. V. Mashkina, *Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds* (All-Union Symp., Abstr. Institute of Organic Synthesis, Riga, 1987), pp. 137–138.
149. A. A. Balandin, M. L. Khidekel and V. V. Patrikeev, *Zh. Obshch. Khim.* **31**, 1876 (1961).
150. J. Rajca, *Pol. J. Chem.* **55**, 775 (1981).
151. R. Mazingo, S. A. Harris, D. E. Wolf, C. E. Hoffhine, N. R. Easton and K. Folkers, *J. Am. Chem. Soc.* **67**, 2092 (1945).
152. A. V. Mashkina, *Kinet. Katal.* **16**, 925 (1975).
153. A. V. Mashkina, *Problems of Catalyst Deactivation* (Institute of Catalysis, Novosibirsk, 1985), pp. 21–38.
154. A. A. Zirka, R. S. Sagitulin, R. M. Masagutov, A. Kh. Sharipov, N. K. Lyapina and A. V. Mashkina, *Kinet. Catal. Lett.* **25**, 171 (1984).
155. T. P. Voskresenskaya, V. N. Yakovleva, V. A. Semikolenov, V. A. Likhobolov and A. V. Mashkina, *Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds*, All-Union Symp. Abstr. (Zinatne, Riga, 1981), pp. 94–96.
156. H. Greenfield, S. Meltin, M. Orchin and J. Wender, *J. Org. Chem.* **23**, 1054 (1958).
157. A. S. Lobach, Yu. M. Shulga, K.-H. Heinrich and M. Varen, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1722 (1988).
158. T. P. Voskresenskaya, V. A. Semikolenov, V. A. Likhobolov, A. P. Shepelin, P. A. Zhdan and A. V. Mashkina, *Kinet. Katal.* **23**, 382 (1982).
159. A. P. Shepelin, P. A. Zhdan, T. P. Voskresenskaya, V. A. Semikolenov, V. A. Likhobolov and A. V. Mashkina, *Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds*, All-Union Symp., Abstr. (Zinatne, Riga, 1981), pp. 99–101.
160. G. L. Veitsman, T. S. Sukhareva and A. V. Mashkina, *Catalysts for the Production and Conversion of Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 70–73.
161. E. Campaigne and J. L. Diedrich, *J. Am. Chem. Soc.* **73**, 5240 (1951).
162. H. S. Broadbent, L. H. Slaugh and N. L. Jarvis, *J. Am. Chem. Soc.* **76**, 1519 (1954).
163. O. Weisser, V. Pekh and Ya. Novak, *Scientific Fundamentals for Catalyst Production* (Nauka, Novosibirsk, 1982), pp. 142–169.
164. S. G. Gagarin, L. E. Slinko, I. G. Petrenko, A. B. Vol-Epshtein, V. N. Grigoriev, E. S. Shpiro and G. V. Antoshin, *Kinet. Katal.* **20**, 1290 (1979).
165. A. A. Zirka, N. K. Lyapina, M. A. Parfenova, R. M. Masagutov, A. Kh. Sharipov, Z. A. Suleimanova, G. L. Ryzhova, Yu. G. Slizhov and A. V. Mashkina, *Neftekhimiya* **28**, 271 (1988).
166. M. Madecsaire, *Tetrahedron* **42**, 5489 (1986).
167. E. Baciocchi, A. Piermattei and R. Ruzziconi, *Synth. Commun.* **18**, 2167 (1988).
168. F. A. Davis, S. G. Lal and D. H. Dupont, *J. Org. Chem.* **53**, 5004 (1988).
169. R. Curci, F. Furia, R. Testi and G. Modena, *J. Chem. Soc., Perkin Trans. 2*, 752 (1974).
170. D. Barnard, L. Bateman and J. J. Cuneen, *Organic Sulfur Compounds* (Pergamon Press, Oxford etc., 1961), Vol. 1, p. 229.
171. P. E. Correa and D. P. Riley, *J. Org. Chem.* **50**, 1787 (1985).
172. A. V. Mashkina and L. B. Avdeeva, *The Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Khimiya, Leningrad, 1964), Vol. 7, pp. 37–39.
173. D. Pope, D. S. Walker and R. L. Moss, *Atmos. Environ.* **19**, 1921 (1978).
174. E. M. Davydova and A. V. Mashkina, *Kinet. Katal.* **12**, 652 (1971).
175. P. S. Maoveev and A. V. Mashkina, *Kinet. Katal.* **9**, 1047 (1968).
176. A. V. Mashkina and V. I. Marshneva, *Kinet. Katal.* **9**, 831 (1968).
177. A. V. Mashkina, *Kinet. Katal.* **27**, 860 (1986).
178. A. V. Mashkina, *Advances in Hydrocarbon Purification from Sulfur and Gas Fractioning* (TsNIINEF-TEKHIM, Moscow, 1980), pp. 118–123.
179. G. I. Golodets and Yu. I. Pyatnitskii, *Catalysis and Catalysts* (Naukova Dumka, Kiev, 1970), Vol. 6, p. 5.
180. G. K. Boreskov, *Catalysis, Problems of Theory and Practice* (Nauka, Novosibirsk, 1987).
181. V. A. Sazonov, V. V. Popovskii and G. K. Boreskov, *Kinet. Katal.* **9**, 312 (1968).
182. V. S. Sheplev, A. V. Mashkina and V. D. Meshcheryakov, *16th Conf. on the Chemistry and Technology of Organic Sulfur Compounds and Sulfurous Oils*, Abstr. (Institute of Organic Synthesis, Riga, 1984), pp. 262–263.
183. E. M. Davydova and A. V. Mashkina, *Kinet. Katal.* **16**, 1510 (1975).
184. A. V. Mashkina, *16th Conf. on the Chemistry and Technology of Organic Sulfur Compounds and Sulfurous Oils*, Abstr. (Institute of Organic Synthesis, Riga, 1984), pp. 51–52.

185. E. M. Davydova and A. V. Mashkina, *Kinet. Katal.* **17**, 141 (1976).
186. A. V. Mashkina, V. S. Sheplev and V. D. Meshcheryakov, *Kinet. Katal.* **25**, 1388 (1984).
187. R. I. Dudina, L. B. Avdeeva, E. M. Davydova and A. V. Mashkina, *Kinet. Katal.* **17**, 664 (1976).
188. R. I. Dudina, L. B. Avdeeva and A. V. Mashkina, *Catalysts for the Production and Conversion of Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 46–49.
189. V. M. Mastikhin, A. V. Mashkina, L. V. Vlasova, E. B. Sekachev and L. B. Avdeeva, *Kinet. Katal.* **18**, 684 (1977).
190. N. I. Polovinkina, P. S. Makoveev and A. V. Mashkina, *Kinet. Katal.* **11**, 1005 (1970).
191. P. S. Makoveev and A. V. Mashkina, *Kinet. Katal.* **10**, 570 (1969).
192. A. V. Mashkina, P. S. Makoveev and N. I. Polovinkina, *Kinet. Katal.* **13**, 124 (1972).
193. A. V. Mashkina, P. S. Makoveev and N. I. Polovinkina, *Reakts. Sposobn. Org. Soedin.* **6**, 24 (1969).
194. A. V. Mashkina, P. S. Makoveev and A. P. Zeif, *Kinet. Katal.* **10**, 823 (1969).
195. P. S. Makoveev and A. V. Mashkina, *Neftekhimiya* **9**, 302 (1969).
196. A. V. Mashkina, T. S. Sukhareva, V. I. Chernov, L. B. Avdeeva, N. I. Polovinkina, E. M. Davydova, G. L. Veitsman, G. A. Spirina and Yu. M. Shchekochikhin, *Organic Sulfur Compounds* (Zinatne, Riga, 1980), Vol. 2, pp. 393–421.
197. L. B. Avdeeva and A. V. Mashkina (Institute of Catalysis, Novosibirsk), *U.S.S.R.* **213,832** (1967); *C.A.* **69**, 51595 (1968).
198. A. V. Mashkina and L. B. Avdeeva, *Neftekhimiya* **8**, 414 (1968).
199. A. V. Mashkina and E. M. Vakurova, *Dokl. Akad. Nauk SSSR* **168**, 821 (1966).
200. M. A. Leadlie and J. V. Howell, *Tetrahedron Lett.*, 785 (1976).
201. A. V. Mashkina, L. B. Avdeeva and V. F. Anufienko, *Kinet. Katal.* **10**, 621 (1969).
202. T. M. Kogan and A. V. Mashkina, *Neftekhimiya* **10**, 230 (1970).
203. L. B. Avdeeva and A. V. Mashkina, *Neftekhimiya* **9**, 779 (1969).
204. A. V. Mashkina, *The Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Vysshaya Shkola, Moscow, 1972), Vol. 9, pp. 301–310.
205. Ya. B. Gorokhovatskii, T. P. Kornienko and V. V. Shalya, *Heterogeneous-Homogeneous Reactions* (Tekhnika, Kiev, 1972).
206. I. I. Ioffe and L. M. Pis'men, *Engineering Chemistry of Heterogeneous Catalysis* (Khimiya, Leningrad, 1972).
207. N. P. Kirik, A. V. Mashkina, A. K. Trofimchuk and L. V. Glushchenko, *Ukr. Khim. Zh.* **47**, 395 (1981).
208. E. Bordighon, L. Cattaline, G. Natile and A. Scatturin, *J. Chem. Soc., Chem. Commun.*, 878 (1973).
209. A. V. Mashkina, *Catalytic Synthesis of Organic Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 42–57.
210. L. B. Avdeeva and A. V. Mashkina, *Neftekhimiya* **14**, 461 (1974).
211. V. I. Berdnikov and P. V. Shastnev, *Kinet. Katal.* **16**, 188 (1975).
212. M. A. Leadlie, K. G. Allum, J. V. Howell and R. C. Pitkethly, *J. Chem. Soc., Perkin Trans. 1*, 1734 (1976).
213. H. B. Henbest and M. G. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, 607 (1974).
214. D. P. Riley and R. E. Shumate, *J. Am. Chem. Soc.* **106**, 3179 (1984).
215. B. R. James, A. Pacheco, S. J. Rettig, J. S. Thorburn and R. G. Ball, *J. Molec. Catal.* **41**, 147 (1987).
216. L. V. Vlasova, G. N. Semyekhin, V. M. Mastikhin and A. V. Mashkina, *Catalysts for the Production and Conversion of Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 54–57.
217. I. V. Kozhevnikov, V. I. Simagina, G. V. Varnakova and K. I. Matveev, *Kinet. Katal.* **20**, 506 (1979).
218. G. M. Batalina and V. A. Proskuryakov, *Zh. Prkl. Khim.*, 2079 (1965).
219. R. I. Dudina, L. B. Avdeeva, L. V. Vlasova, *Neftekhimiya* **19**, 462 (1979).
220. A. V. Mashkina, G. V. Varnakova, L. M. Zagryatskaya, Z. A. Suleimanova, R. M. Masagutov, A. Kh. Sharipov, V. N. Yakvoleva, L. V. Vlasova and N. P. Kirik, *Kinet. Katal.* **22**, 607 (1981).
221. G. V. Varnakova, A. V. Mashkina, N. P. Kirik, R. M. Masagutov, A. Kh. Sharipov, L. M. Zagryatskaya and Z. A. Suleimanova, *Kinet. Katal.* **25**, 837 (1984).
222. G. V. Varnakova, A. V. Mashkina, R. M. Masagutov, A. Kh. Sharipov, N. P. Kirik, L. M. Zagryatskaya and Z. A. Suleimanova, *Kinet. Catal. Lett.* **29**, 33 (1985).
223. A. V. Mashkina, R. S. Sagitullin and T. A. Manykina, *Neftekhimiya* **25**, 96 (1985).
224. A. V. Mashkina, A. N. Gartsman, A. Kh. Sharipov, R. M. Masagutov, N. P. Kirik and Z. A. Suleimanova, *Neftekhimiya* **23**, 552 (1983).
225. V. M. Mastikhin, L. B. Avdeeva and M. A. Fedotov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 266 (1977).
226. N. A. Geraseva, A. A. Shklyayev, A. S. Zanina and V. F. Anufrienko, *Zh. Strukt. Khim.* **19**, 660 (1978).
227. A. V. Mashkina, A. Kh. Sharipov, N. K. Lyapina, R. M. Masagutov and Z. A. Suleimanova, *Neftekhimiya* **24**, 106 (1984).



228. K. B. Yatsimirski (Ed.), *Advances in the Chemistry of Coordination Compounds* (Naukova Dumka, Kiev, 1975).
229. B. R. James, F. T. Ng and G. L. Rempel, *Can. J. Chem.* **47**, 4521 (1969).
230. K. Ogura, M. Yamashita and G. Tsuchihashi, *Synthesis*, 395 (1975).
231. E. N. Karaulova, *The Chemistry of Oil Sulfides* (Nauka, Moscow, 1970).
232. V. V. Puchkova, E. N. Guryanova, R. R. Shifrina and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR* **207**, 886 (1972).
233. J. E. McCaskie, P. L. Chang, T. R. Nelsen and D. C. Dittmer, *J. Org. Chem.* **38**, 3963 (1973).
234. R. L. Moore and R. A. Trimble (Shell Development Co.), U.S. **2,471,077** (1949); *C.A.* **43**, 7512 (1949).
235. J. H. Boyd (Phillips Petroleum Co.), U.S. **2,440,671** (1948); *C.A.* **42**, 7341 (1948).
236. K. Itabashi, *Yuki Gosei Kagaku Kyokai Shi* **18**, 475 (1960); *C.A.* **54**, 19466 (1960).
237. V. F. Odyakov, K. I. Matveev, N. N. Shushilova and A. V. Mashkina, *Kinet. Katal.* **15**, 76 (1974).
238. R. A. Virobyants, M. A. Nechayeva and R. S. Gareev, *Zh. Prikl. Khim.* **37**, 1851 (1964).
239. A. V. Mashkina and V. I. Chernov, *The Chemistry of Sulfur-Organic Compounds Contained in Oils and Their Products* (Vysshaya Shkola, Moscow-Leningrad, 1964), Vol. 7, pp. 7-15.
240. N. M. Sinityn, A. V. Mashkina and Yu. A. Savostin, *Neftekhimiya* **7**, 785 (1967).
241. A. V. Mashkina and Yu. A. Savostin, *Neftekhimiya* **7**, 781 (1967).
242. A. V. Mashkina, S. A. Lange, Zh. A. Evdokimova, Yu. R. Gorbenko, T. P. Aleksandrova and L. B. Avdeeva, *Neftekhimiya* **12**, 390 (1972).
243. A. V. Mashkina, N. T. Kulishkin and V. P. Kornilova, *Kinet. Katal.* **16**, 697 (1975).
244. T. P. Voskresenskaya, V. D. Chinakov, V. M. Nekipelov and A. V. Mashkina, *React. Kinet. Catal. Lett.* **32**, 359 (1986).
245. I. I. Frolova, V. A. Semikolenov, V. A. Likholobov and Yu. I. Yermakov, *Catalysts for the Production and Conversion of Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 81-84.
246. G. L. Veitsman, A. V. Mashkina and T. S. Sukhareva (Institute of Catalysis, Siberian Branch, USSR Academy of Sciences), U.S.S.R. **341,799** (1972); *C.A.* **78**, 43257 (1973).
247. T. E. Bezmenova, A. V. Mashkina and V. N. Yakovleva (Institute of Physical-Organic Chemistry and Coal Chemistry, Kiev; Institute of Catalysis, Novosibirsk), U.S.S.R. **1,079,651** (1984); *C.A.* **101**, 54908 (1984).
248. T. E. Bezmenova, A. V. Mashkina and V. N. Yakovleva, *Kinet. Katal.* **25**, 56 (1984).
249. N. T. Kulishkin, A. V. Mashkina, N. E. Buyanova, A. P. Karnaukhov, I. D. Ratner and L. M. Plyasova, *Kinet. Katal.* **12**, 1539 (1971).
250. N. T. Kulishkin, A. V. Mashkina and N. E. Buyanova, *Kinet. Katal.* **14**, 1068 (1973).
251. N. T. Kulishkin and A. V. Mashkina, *Kinet. Katal.* **16**, 1099 (1975).
252. N. T. Kulishkin, A. V. Mashkina, N. E. Buyanova and V. T. Rybak, *Kinet. Katal.* **17**, 267 (1976).
253. N. T. Kulishkin, V. N. Yakovleva, Yu. A. Savostin and A. V. Mashkina, *Catalysts for the Production and Conversion of Sulfur Compounds* (Institute of Catalysis, Novosibirsk, 1979), pp. 58-61.
254. Yu. A. Savostin, N. T. Kulishkin and A. V. Mashkina, *ibid.*, pp. 62-65.
255. V. P. Kornilova and T. S. Sukhareva, *ibid.*, pp. 66-69.
256. P. N. Rylander, *Catalytic Hydrogenation of Palladium Metals* (Academic Press, New York etc., 1967).
257. G. D. Chukin, B. V. Smirnov, V. I. Malevich, M. V. Landau, V. Ya. Kruglikov and N. V. Goncharova, *Kinet. Katal.* **17**, 1273 (1976).
258. A. V. Mashkina, V. N. Yakovleva, N. E. Buyanova and Z. A. Dovbii, *Kinet. Katal.* **23**, 58 (1982).
259. A. V. Mashkina and Yu. A. Savostin (Institute of Catalysis, Siberian Branch, USSR Academy of Sciences), *Brit.* **1,260,037** (1972); *C.A.* **76**, 99500 (1972).
260. S. L. Kiperman, *Catalytic Hydrogenation, Ser. Studies Surface Sci. Catal.*, Vol. 27 (Elsevier, Amsterdam etc., 1986), pp. 1-52.

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