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NOTE

Catalytic Synthesis of Methylmercaptan by Selective Reduction of Dimethyldisulfide

Industrially, thiochemistry is related to the synthesis of about 30 compounds shared out between mercaptans, sulfides, polysulfides, sulfones or sulfoxides, thioacids, and thioesters. These sulfur containing molecules are used in increasing quantities in agrochemicals, pharmaceutical products, petrochemicals, lubricants, cosmetics, and gas odorants. Among them, mercaptans are the most important because they are very often utilized as starting materials for the synthesis of the other thiocompounds. Lower molecular weight alkanethiols, e.g., methanethiol, ethanethiol, propanethiol, and butanethiol, are used as intermediates in the manufacture of agricultural chemicals including insecticides, acaricides, herbicides, and defoliants. Besides these applications, a large amount of methanethiol is produced because of its utilization in the first step of the commercial synthesis of methionine, an amino acid poultry feed supplement. Industrially, methylmercaptan is currently prepared by direct thiolation of methanol over alkali metal salts or oxides supported on alumina and acidic catalysts (1). Methylmercaptan is characterized by its obnoxious odor, its low boiling point (278 K), its highly flammable properties, and its drastic toxicity. This gas is shipped in various sizes of pressure and copper free alloy vessels and metal drums should be unloaded and handled carefully to prevent leaks and odor from escaping. In the future it could be expected that the transportation of such a hazardous compound will be faced with increasing environmental requirements. For these multiple reasons, the transformation of CH_3SH into a safer compound like alkali mercaptides has been already envisaged. Starting from this organic salt, the back formation of CH_3SH requires only a hydrolysis step in a slightly acidic media. However, this step leads to the unavoidable formation of alkali salt wastes. Another possibility would be to convert CH_3SH into dimethyldisulfide (DMDS, boiling point 383 K) by air oxidation in the presence of a base at room temperature (2). As DMDS is already produced on a large scale for sulfiding purposes, this alternative could be interesting only if the selective catalytic hydrogenolysis of the S–S bond could be achieved with a low hydrogen consumption. As a matter of fact, the utilization of conventional reductive organic reagents such as hydrides (3), trivalent phosphorus compounds (4), hydroxides, cyanide ions (5), and hydrazine derivatives (6) cannot be envisaged in industrial plants. Recently, we reported that sulfide catalysts may catalyze the reduction of aryl disulfides into their corresponding thiols at a temperature as low as 433 K and under a hydrogen pressure of only 2280 Torr ($1 \text{ Torr} = 133.33 \text{ N m}^{-2}$) (7). Under these mild conditions the thiol selectivity was 100% even at 100% conversion. This unexpected high selectivity was ascribed to the employed mild experimental conditions which do not allow the hydrodesulfurization of the C_{sp2}–S bond. For aliphatic thiols lower selectivities are expected since the C_{sp3}–S is weaker than the C_{sp2}–S bond and because primary mercaptans are known to easily condense into the corresponding sulfides. The aim of this work was to explore the ability of sulfide catalysts to transform DMDS into CH_3SH.

The catalysts studied in this work were mostly Ni, Co, Mo, CoMo, NiMo, and NiW sulfides supported on a high surface area ($230 \text{ m}^2/\text{g}$) γ alumina. These systems were chosen because they are known to possess hydrogenating properties. Table 1 summarized the catalyst composition. The metal loading expressed in at/m^2 is almost the same whatever the nature of the solid and corresponds to the optimized concentration which leads to a highly dispersed sulfide phase. All these solids are commercially available in their oxidic form. Thus they were sulfided by treating them in a 85% H_2–15% H_2S mixture at 673 K for 4 h. This procedure allows the transformation of the oxide phases into the corresponding sulfides (8). The catalytic properties were determined in a continuous plug flow microreactor equipped with an automatic on-line analysis. The reaction was carried out at 473 K using a molar ratio $H_2/\text{DMDS} = 2$ (partial pressure of $\text{DMDS} = 15$ Torr) diluted in nitrogen. The composition of the gas phase was determined by gas chromatography with a satisfying carbon mass balance. The specific activity was calculated according to the pseudo-first-order equation after 16 h time on stream, the catalyst deactivation being not really significant. The reproducibility of the experiments was within 6–8%.

Figure 1 reports the activity and the selectivity toward CH_3SH formation of the different solids. In this set of experiments, the total conversion was kept constant at $40 \pm 4\%$ by adjusting either the catalyst weight or the reactant flow rate. The formation of CH_4 was not observed and only CH_3SH and CH_3–S–CH_3 (DMS) were detected. These data show

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TABLE 1

Catalyst Composition

Catalyst	Ni	Co	Mo	CoMo	NiMo	NiW
Metal loading (10^{+18} at/m^2)	1.0	1.0	2.3	Co : 1.0 Mo : 2.3	Ni : 1.0 Mo : 2.3	Ni : 1.0 W : 2.1

that the CH_3SH selectivity does not vary in a large extent with the nature of the catalyst under investigation and approximately half of the initial DMDS leads to CH_3SH. By contrast, significant variations of activity were detected. The Co or Ni promoted molybdenum or tungsten sulfides were about 3 times more active than the alumina supported monocomponent systems. This behavior resembles the well known synergy effect observed in the hydrodesulfurization of thiophene-like molecules or in the hydrogenation of aromatics (9).

In order to clarify the possible pathways leading to CH_3SH and DMS, the evolution of their yields with the DMDS conversion was determined. This study was carried out on the alumina supported NiMo phase which presents both the highest activity and selectivity. The yield–conversion plot schematized in Fig. 2 indicates that no reaction products other than CH_3SH and DMS are present even when the DMDS conversion attained 100%. Data also evidence that the initial CH_3SH selectivity equals 100% because DMS is not produced at low conversion. Moreover, the DMS selectivity increases as far as the DMDS conversion goes up whereas the CH_3SH selectivity follows an opposite trend. This strongly suggests that DMS is formed by the consecutive condensation of the primary product and reaction [1] depicts the formal mechanism of the transformation of DMDS:

$$CH_3SSCH_3 + H_2 \rightarrow 2\,CH_3SH \rightarrow CH_3SCH_3 + H_2S. \quad [1]$$

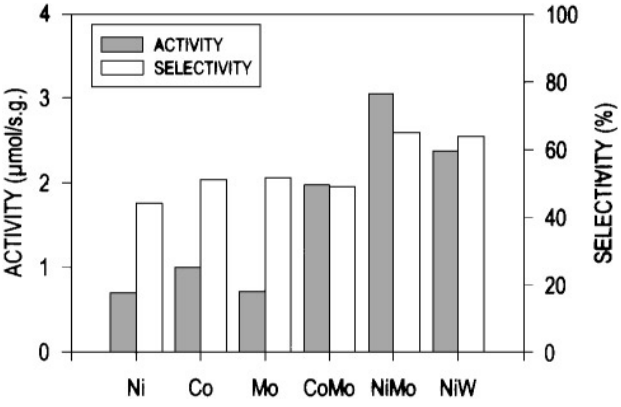

FIG. 1. Catalytic properties of various sulfided phases for the transformation of DMDS at 473 K.

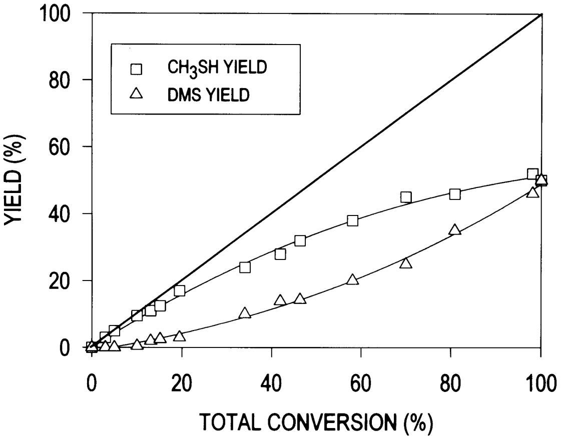

FIG. 2. Yield–conversion diagram observed on the alumina supported NiMo catalyst (Reaction temperature = 473 K).

Assuming a Langmuir Hinshelwood-type mechanism, the first hydrogenolysis step should require the chemisorption of both hydrogen and DMDS. From a previous study dealing with the catalytic reduction of aryldisulfides it was suggested that the presence of both SH groups and coordinatively unsaturated metal ions (CUS) was a necessary requirement for the S–S bond breaking (7). A mechanism was proposed in which the reaction may proceed via the addition of a $H^{\delta+}$ species (fixed on a sulfur anion) and of a $H^{\delta-}$ adsorbed on a coordinatively sulfur deficient metal ion. Extended Hückel calculations suggested also that the polysulfide–CUS interaction via the lone electron pair of the sulfur atoms is the favorable route for the chemisorption of the organic molecule (10). Furthermore, it is generally admitted that the alumina support does not participate in the activation of hydrogen. Therefore it is proposed that the first hydrogenolysis step leading to CH_3SH takes place only on the sulfided phase where hydrogen may be activated.

The interaction of C_2H_5SH with an alumina support was studied by Sugioka *et al.* (11). From IR experiments they showed that thiol chemisorption gave rise to a band at 1268 cm^{-1} ascribed to the vibration of Al–S–CH_3 species and to a concomitant broadening of the hydroxyl groups absorption in the range 3000–3500 cm^{-1}. As the SH vibration of the organic molecule was not observed, they concluded that ethanethiol dissociatively adsorbed at the surface leading to the formation of an OH and thiolate species. Moreover, these authors claimed that these species might be the intermediates of the formation of diethylsulfide. Similar results were obtained by several authors (12, 14) for the adsorption of CH_3SH. Using various oxides with different acid–base properties they demonstrated that the most effective catalysts for the formation of DMS are those containing pairs of acid–base centers namely, strong Lewis acid sites and medium basic sites. According to these studies the

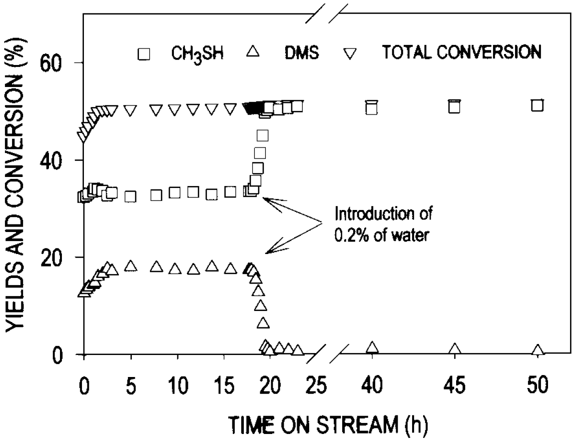

FIG. 3. Influence of the presence of water on the conversion of DMDS and product distribution observed on the sulfided NiMo catalyst.

observed formation of DMS should occur on the fraction of the alumina support not covered by the sulfided phase. Therefore, the formation of DMS may be limited by poisoning the acidic Lewis aluminium site of the support and such a poison should have a stronger basicity than CH_3SH. However, the use of nitrogen containing molecules should be avoided since they are known to strongly inhibit the hydrogenating properties of sulfides (14). Another potential inhibitor such as water would be interesting for our purpose since this molecule is known to adsorb on inorganic supports and because water is easily available in all industrial plants. Figure 3 shows the evolution of the total conversion and of the CH_3SH and DMS yields as a function of the reaction time. After about 16 h time on stream, 0.2% of water ($P_{H_2O} = 1.5$ Torr) was introduced in the feed. Surprisingly the addition of water almost completely killed the condensation reaction without modifying the total conversion. Results reported in Table 2 evidence that this inhibiting effect is still efficient at high conversion. This result suggests that water inhibits the acid–base centers of the alumina support without affecting the amount of the hydrogenating sites of the sulfided phase.

To sum up, the reduction of DMDS into CH_3SH is selectively achieved under mild experimental conditions using alumina supported sulfided catalysts. This study points out the ability of transition metal sulfides to catalyze reactions involving the conversion of sulfur containing molecules without C–S bond cleavage. This property makes the sulfide catalysts interesting for organic synthesis applications, particularly for the hydrogenation of thiocompounds where more effective hydrogenating solids like metals would be poisoned by the reactants.

TABLE 2

CH_3SH Selectivity and Total Conversion in the Presence of 0.2% of Water

DMDS conversion (%)	29	40	58	79.2	91	99
CH_3SH selectivity (%)	100	100	98	97	95.6	96.3

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Emmanuel Cadot*
Michel Lacroix*
Michèle Breysse*
Emmanuel Arretz†

**Institut de Recherches sur la Catalyse*
2 Avenue Albert Einstein
69626 Villeurbanne Cedex, France
†*Groupement de Recherches de Lacq*
B.P. N° 34
64170 Lacq, France

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