

HYDROGENATION-DEHYDROGENATION AND CLEAVAGE FUNCTIONS OF HYDROREFINING CATALYSTS STUDIED BY THE REACTION OF TETRAHYDROTHIOPHENE

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The reaction of tetrahydrothiophene in a stream of nitrogen was used to study the relations between dehydrogenation and C—S cleavage reactions on sulphided Co—Mo/Al₂O₃ catalysts. The course of the reaction was compared for Co—Mo catalysts supported on alumina and activated carbon, for alumina alone as well as for a Pt/C catalyst. The effect of substitution of nitrogen for hydrogen, of the addition of water to the feed, of pre-sulphidation of catalysts and their deactivation by coking on the rate and selectivity of the reaction were also investigated. The results showed that hydrogenation-dehydrogenation and dehydrosulphurization activity of the sulphide catalysts have the same origin. Hydrogen accelerates dehydrosulphurization on the sulphide catalysts by removing sulphur and unsaturated hydrocarbons formed on catalyst surface by C—S bond cleavage reactions.

Sulphide catalysts catalyze hydrogenation-dehydrogenation reaction and C—S bond cleavage¹⁻⁴. The relation between these catalytic functions is, however, still unclear. Desikan and Amberg⁵ poisoned a Co—Mo catalyst by sulphur- and nitrogen-containing compounds and suggested that hydrogenation proceeds on strongly acidic and hydrodesulphurization on weakly acidic sites. Lee and Butt⁶ found that poisoning of catalysts by pyridine leads first to parallel decrease of both hydrogenation and cleavage activity, but after strong poisoning hydrogenation reaction is more sensitive to pyridine. The authors believe that the assumption about sites of two types is more substantiated. Pirotte and coworkers⁷ advocated the model of different sites for hydrogenation and hydrodesulphurization on the basis of different magnitude of contact synergic effect for both reactions. Hagenbach and coworkers⁸ found for a series of Co—Mo catalysts that maximal rates of hydrogenation and cleavage are attained at the same Co/Mo ratio, from which it was concluded that both reactions are interrelated and proceed on identical sites. López and Kraus⁹ reported on the parallelity in activities of several Ni—Mo and Ni—W catalysts for olefin hydrogenation, benzothiophene hydrodesulphurization and hydrodenitrogenation, speaking for the same catalytic site in these reactions.

In characterizing a given catalyst, the evaluation of its activity for C—S bond cleavage is more difficult compared with hydrogenation-dehydrogenation activity. Hydrodesulphurization of aromatic sulphur-containing compounds is not a suitable model reaction for determining cleavage activity. The reaction involves both hydrogenation-dehydrogenation and cleavage elemental steps which are interrelated in a complicated way and cannot be separated by kinetic analysis¹⁰. The relation between these both functions can be, however, examined easier by using parallel dehydrogenation and dehydrosulphurization of the non-aromatic tetrahydrothiophene, in the absence of

hydrogen. The reaction has attracted attention from other reasons (technology of thiophene production)¹¹⁻¹⁴. Tetrahydrothiophene desulphurization in hydrogen was studied in relation to the mechanism of thiophene hydrodesulphurization¹⁵⁻¹⁸. Dehydrosulphurization of tetrahydrothiophene alone on acidic catalysts not containing metals was also reported⁴.

The aim of the present work was to define the relation between the activities of hydrorefining catalysts for hydrogenation and C—S cleavage by the study of dehydrogenation and desulphurization of tetrahydrothiophene. For that reason, the course of the reaction on different catalysts and relationship between both activities and poisoning by coke formation and the presence of hydrogen and water were examined.

EXPERIMENTAL

Catalysts used are listed in Tables I and II and were of four basic types: a) commercial hydrorefining catalysts of Co—Mo/Al₂O₃ type, b) laboratory Co—Mo hydrorefining catalysts supported on either alumina or activated carbon, c) alumina alone, d) platinum on activated carbon. The hydrorefining catalysts were used as oxides or they were pre-sulphided by H₂S/H₂ (1 : 10) mixture at 450°C, using the already reported procedure¹⁹. The catalysts were stored in air. The pre-sulphided form of the catalyst is further designated as (s). The acid-base catalysts were used without further treatment, only in some experiments the catalysts were activated in situ under an inert atmosphere at 500°C.

The reactions studied were carried out either as parallel dehydrogenations and dehydrosulphurization of tetrahydrothiophene in nitrogen or as hydrodesulphurization of tetrahydrothiophene in hydrogen. In both cases, experiments differed only in the gas feeding to the reactor. A tubular, integral flow reactor worked under atmospheric pressure and the mean pressure was 100 kPa. A solution of 20 mole % of tetrahydrothiophene in toluene was charged with a piston pump to gas stream such that partial pressures were 90 kPa for the gas (nitrogen and hydrogen), 8 kPa for toluene and 2 kPa for tetrahydrothiophene. Temperature of a condenser on the reactor outlet was -20°C and liquid products were analysed chromatographically (1.7 m long column, 3 mm i.d., 20% Apiezon L on Rysorb BLK (Lachema Brno, Czechoslovakia), temperature 134°C, hydrogen as carrier gas). It was proved that toluene does not react under given experimental conditions and was thus taken as internal standard in chromatographic analysis. Conversions were defined as follows: total tetrahydrothiophene conversion $x(\text{THT}) = (n^0(\text{THT}) - n(\text{THT}))/n^0(\text{THT})$, the conversion of tetrahydrothiophene to thiophene $x(\text{T}) = n(\text{T})/n^0(\text{THT})$, and the conversion of tetrahydrothiophene to hydrogen sulphide $x(\text{HS}) = n(\text{HS})/n^0(\text{THT})$, where n^0 and n is the number of moles in the feed and the products, respectively, THT is tetrahydrothiophene, T stands for thiophene and HS for hydrogen sulphide.

Procedure. The known amount of catalyst, W (0.02—10 g), placed in the reactor was heated to the reaction temperature in a stream of reacting gas (nitrogen or hydrogen) and the liquid was fed with the rate $F = 9 \cdot 10^{-3} \text{ mol h}^{-1}$ (THT). The condenser content was discharged after 7 min from the start of feeding (volume of the liquid charged was about 1 ml) and this portion of the liquid was not analysed. Then, samples were collected for 15 min, withdrawn and analysed. Time of experiment t (min) was taken from the start of the feeding and the composition of each integral sample was assigned to the time t_1-8 where t_1 is time of withdrawal of i -th sample.

In the study of the effect of water on the reaction in nitrogen, the first hour of the experiment was as usual. Then, gas paths were changed-over without interrupting the feed, and nitrogen was

led through the saturator containing water cooled to 5°C before entering the reactor. Partial pressure of water in the reaction mixture was approx. 0.9 kPa. After another hour, in which 4 samples were withdrawn, the saturator was cut-off from the nitrogen line and the reaction was followed for another 1 h.

RESULTS

Reaction of tetrahydrothiophene in nitrogen. The activity of the catalysts decreased during experiment, depending on time t . With respect to the rate of deactivation, all

TABLE I

Activity k and selectivity S of hydrorefining catalysts in the parallel dehydrogenation and dehydrosulphurization of tetrahydrothiophene in nitrogen at 400°C

Catalyst	Origin	k^a		S^b	
		oxide	sulphided	oxide	sulphided
Co-Mo/Al ₂ O ₃	Cherox 3601 ^c 3,5% CoO, 14% MoO ₃	—	1.7	—	0.6
Co-Mo/Al ₂ O ₃	Girdler G-35 ^d 3,5% CoO, 10% MoO ₃	1.2	2.7	0.6	0.6
Co/Al ₂ O ₃	laboratory 3% CoO	0.7	0.6	0.05	0.05
Mo/Al ₂ O ₃	laboratory 10% MoO ₃	0.6	1.1	1.0	1.0
Co-Mo/Al ₂ O ₃	laboratory 3% CoO, 10% MoO ₃	1.3	3.6	1.0	1.0
Co/C	laboratory 3% CoO	—	2.6	—	0.7
Mo/C	laboratory 70% MoO ₃	—	3.2	—	2.0
Co-Mo/C	laboratory 3% CoO, 70% MoO ₃	—	7.8	—	1.0
Pt/C	laboratory 20% Pt	2.3	—	4.0	—
C	CAL 12-40 ^e	0	—	—	—

^a Rate constant of the first order equation for tetrahydrothiophene consumption, mmol h⁻¹ g⁻¹;

^b slopes $a(T)/a(HS)$ of the lines in composition diagram (examples see Fig. 2); ^c Chemical Works, Litvínov, Czechoslovakia, ^d Süd Chemie, A.G., München, F.R.G.; ^e activated carbon, Pittsburgh Activated Carbon, U.S.A.

the catalysts can be divided into two groups. The first group includes all the catalysts from Table I having alumina as support, except for Co/Al₂O₃ sample. Typical behaviour of the catalysts of this group is demonstrated on deactivation of Co-Mo/Al₂O₃ Cherox 3601(s) catalyst shown in Fig. 1. Catalysts of the second group are deactivated more slowly, at the rates which are comparable with the deactivation of Mo/C(s) catalyst in Fig. 1. The second group includes all the catalysts from Table II, the catalysts supported on activated carbon from Table I and the Co/Al₂O₃ catalyst. The exception is the alumina Cherox 3300 which deactivated distinctly more slowly than did the catalysts of the second group. The rate of activity decrease was the same for both oxide and sulphide catalysts from Table I. As found for Co-Mo/Al₂O₃ Cherox 3601(s) and Girdler G-35(s) catalysts by comparing the deactivation rates in toluene and nonane as the feed solvents, the catalysts are deactivated at approximately the same rate.

For comparison of the catalyst activity we used percentual conversion in time $t = 90$ min, in which time the rate of deactivation was relatively slow. In the case of Co-Mo/Al₂O₃ Cherox 3601(s) and laboratory Mo/C(s) catalysts, we changed weighed amounts of the catalysts. We found that the dependence of $x(\text{THT})$ on space time W/F obeys the first order kinetic equation in the $x(\text{THT})$ range from 5 to 95 per cent. The experiments with the other catalysts were made with the catalysts of the same weighed amount each; for the catalysts listed in Table I it was 1.3 g and for those from Table II it was 3.0 g. The conversions $x(\text{THT})$ in time $t = 90$ min were used to calculate rate constants according to the first order rate equation. These are presented in Tables I and II.

The selectivity of catalysts did not change by deactivation, which is demonstrated on the diagram of molar composition of the reaction mixture in Fig. 2 (molar frac-

TABLE II

Activity k and selectivity S in the parallel dehydrogenation and dehydrosulphurization of tetrahydrothiophene in nitrogen at 400°C

Alumina	k^a	S^b
Cherox 3300 ^c	1.0	0.02
Pre-sulphided Cherox 3300	1.3	0.02
Spheralite SCS 250 ^d	1.6	0.02
Spheralite SCS 79 ^d	0.2	0.02
Spheralite SCS 9 ^d	0	—

^a Rate constant of the first order equation for tetrahydrothiophene consumption, $\text{mmol h}^{-1} \text{g}^{-1}$;

^b slopes $a(\text{T})/a(\text{HS})$ of the lines in composition diagram (examples see Fig. 2); ^c Chemical Works, Litvínov, Czechoslovakia; ^d Rhone-Poulenc Specialities Chimiques, France.

tions: $a(T) = x(T)$, $a(HS) = x(HS)$, $a(THT) = 1 - x(THT)$). Composition points obtained in the course of deactivation form the curve in the composition triangle which is identical with the dependence determined from the composition of initial samples vs different weighed amounts. In general, time of experiments was 1.5 h and the conversion $x(THT)$ decreased in average to half the original value (see Fig. 1). In selected experiments with Co-Mo/Al₂O₃ Cherox 3601(s), laboratory Mo/C(s) and Al₂O₃ Cherox 3300 catalysts, the product composition was followed for 5 h, and the constant selectivity was thus verified over broader range of deactivation. Thus, for example, with 1.3 g of Co-Mo/Al₂O₃ Cherox 3601(s) catalyst, its deactivation was followed starting at $x(THT)$ 95% to the final 20% and the product composition in this region was found to follow the curve determined with the use of fresh samples (see Fig. 2).

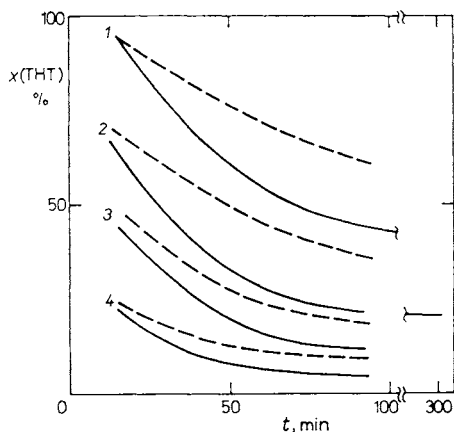


FIG. 1

Catalyst deactivation in the reaction of tetrahydrothiophene in nitrogen at 400°C. — — — Mo/C(s), — Co-Mo/Al₂O₃ Cherox 3601(s), weighed amounts W : 1 1.3 g, 2 0.7 g, 3 0.4 g, 4 0.2 g

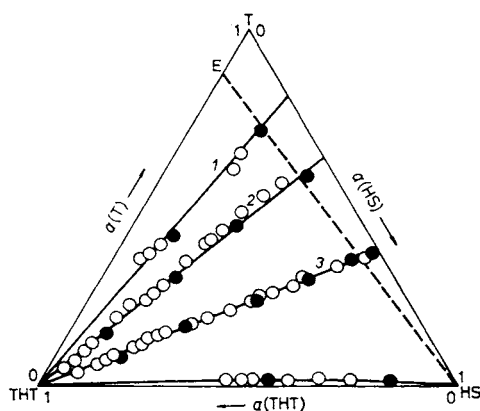


FIG. 2

Composition of the reaction mixture in the reaction of tetrahydrothiophene in nitrogen at 400°C. $a(i)$ molar fractions, THT tetrahydrothiophene, T thiophene, HS hydrogen sulphide; ● composition for different fresh catalyst samples (first integral sample), ○ composition during deactivation (only typical points are plotted); catalysts: 1 Pt/C, 2 Mo/C(s), 3 Co-Mo/Al₂O₃ Cherox 3601(s), 4 Al₂O₃ Cherox 3300; partial equilibrium THT-T-H₂: in hydrogen — the line E-HS; in nitrogen — the line T-HS

With respect to the selectivity, the catalysts can be divided into four groups, the behaviour of which is shown on examples in Fig. 2. All the aluminas from Table II and the catalyst $\text{Co}/\text{Al}_2\text{O}_3$ from Table I behaved similarly as Al_2O_3 Cherox 3300 catalyst in Fig. 2. The only reaction which took place on these catalysts was dehydro-sulphurization, and the amount of thiophene detected in the reaction mixture was thus very small; the slope $S = a(\text{T})/a(\text{HS}) = x(\text{T})/x(\text{HS})$ in the linear part of the curve in Fig. 2 was smaller than 0.05 (see Tables I and II).

Typical behaviour of the hydrorefining catalysts from Table I, except for Mo/C , Pt/C , and $\text{Co}/\text{Al}_2\text{O}_3$ catalysts, is demonstrated by the selectivity of $\text{Co-Mo}/\text{Al}_2\text{O}_3$ Cherox 3601(s) catalyst shown in Fig. 2. The slope S for this catalyst was 0.6; for the other catalysts of this group the slope was 0.6–1.0 (see Table I). Selectivities of the oxide and sulphide catalysts were found to be the same. The important feature of the reaction was that on increasing space time W/F on these catalysts, the content of thiophene in the products did not change after all the tetrahydrothiophene had reacted. The reaction of tetrahydrothiophene proceeds here, following the scheme of two parallel irreversible reactions.

In the case of Mo/C ($S = 2.0$) and Pt/C ($S = 4.0$) catalysts, dehydrogenation is prevailing over dehydro-sulphurization and also here thiophene is stable product under experimental conditions.

The effect of water on the reaction of tetrahydrothiophene in nitrogen was studied on $\text{Co-Mo}/\text{Al}_2\text{O}_3$ Cherox 3601(s) and Al_2O_3 Spheralite SCS 250 catalysts. The presence of water did not exert any effect on the activity, stability and selectivity of these hydrorefining catalysts. In the case of alumina alone, the reaction was strongly slow down by water, as shown on example in Fig. 3.

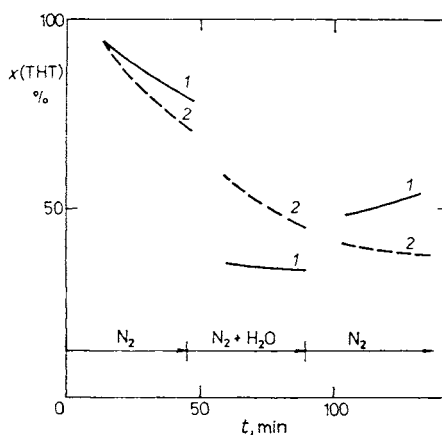


FIG. 3

The effect of water in the feed (partial water pressure 0.9 kPa) on the reaction of tetrahydrothiophene in nitrogen at 400°C. 1 Al_2O_3 Spheralite SCS 250, 2 $\text{Co-Mo}/\text{Al}_2\text{O}_3$ Cherox 3601(s)

Reaction of tetrahydrothiophene in hydrogen. The effect of hydrogen on the course of the reaction was examined in two steps. The first series of experiments was performed with the use of standard weighed amounts of the catalysts Co-Mo/ Al_2O_3 Cherox 3601(s) (1.3 g), Co/ Al_2O_3 (s) (non-standard amount 1.0 g), and Al_2O_3 Cherox 3300 (3.0 g).

After 1 h-reaction in nitrogen, the gas was displaced by hydrogen, four integral samples were withdrawn during 1 h, the gas was substituted again for nitrogen and the reaction was followed for another 1 h. The characteristics of the reaction, *i.e.* activity, stability and selectivity on alumina was not affected by hydrogen. With Co-Mo/ Al_2O_3 catalyst, the percentual conversion $x(\text{THT})$ increased immediately (already in the initial sample) to 100% and the conversion $x(\text{T})$ decreased below 1 per cent. After change-over to nitrogen, the activity decreased instantaneously and the catalyst continued to be deactivated at the usual rate. The catalyst was partially regenerated in hydrogen. With Co/ Al_2O_3 (s) catalyst, the reaction was affected by hydrogen, but only very little. Thus, for example, with 1 g sample of the catalyst, conversions $x(\text{THT})$'s were: the conversion in nitrogen 55, after 1 h in nitrogen 38, after change-over to hydrogen 43, after 1 h in hydrogen 47, after change-over to nitrogen 38, and after another 1 h in nitrogen 26 per cent.

In the second stage, the weighed amounts of both commercial catalysts were changed in such a way that conversions $x(\text{THT})$ were within the range 5 to 95 per cent. For the oxide forms, the amounts tested were 0.05 and 0.11 g, and for the sulphide catalysts they were 0.02 g and 0.04 g. It was found that during these experiments the activity did not change essentially (very small decrease for pre-sulphided samples and very small increase for oxide samples). In the conversion region measured, $x(\text{THT})$ 10–70%, conversion $x(\text{T})$ was less than 1 per cent. The first order equation (the validity of which was verified by measuring the whole integral curve for Girdler G-35(s) catalyst) was used to calculate the rate constants presented in Table III.

DISCUSSION

Gaseous products of dehydrosulphurization were not analysed in this work. Based on the studies by other authors, the product formed on hydrorefining catalysts is a mixture of butadiene, butenes and butane^{16,20}. Hydrogen needed for hydrogenation of butadiene to butenes and butane originates from the dehydrogenation of tetrahydrothiophene to thiophene or from coke formation. In order to exclude possible stoichiometric coupling of dehydrogenation with dehydrosulphurization, which would otherwise determine the selectivity, we made experiments with Pt/C catalyst. The high selectivity S of this catalyst (Table I and Fig. 2) confirmed that the extent of dehydrosulphurization is not determined by the amount of hydrogen produced by dehydrogenation.

The activity decrease observed for the catalysts during the reaction in nitrogen is caused by surface coking. The source of the coke are obviously unsaturated products of dehydrosulphurization, in accordance with the results obtained in butadiene cracking in helium at 400°C, using hydrorefining catalysts²¹ as well as with the activity decrease reported for the reaction of tetrahydrothiophene alone in the absence of solvent¹⁶. However, certain role of solvents cannot be excluded; this is supported by the results obtained by Scaroni and coworkers²² concerning coking of hydrorefining catalysts by cracking of anthracene.

The hydrorefining catalysts on alumina deactivated faster than aluminas, since coke formation on these catalysts is accelerated by the dehydrogenation activity of the phase supported. The same effect was observed by Scaroni and coworkers²² in cracking of anthracene in nitrogen on Co-Mo/Al₂O₃, and by Laine and coworkers²¹ in cracking of butadiene on Ni-Mo/Al₂O₃ and on Al₂O₃. Our results for the catalysts supported on carbon further show that the rate of deactivation of the supported phase itself is not greater than that of alumina (as shown in Table I, the activated carbon support is inactive for tetrahydrothiophene cracking and does not participate apparently also in coke formation). Therefore, in the case of mixed Co-Mo/Al₂O₃ and Mo/Al₂O₃ catalysts, there is positive synergic effect between the support and the supported phase in coke formation. In the case of Co/Al₂O₃ catalyst, the supported phase is little active for already known reasons (strong interaction with the support, *cf.*²³); this explains why the catalyst is deactivated similarly as alumina alone. In accordance with this fact, the catalyst showed very low selectivity *S* and its activity was not sensitive to sulphidation (Tables I and II) and to the substitution of hydrogen for nitrogen.

Hydrorefining catalysts activate hydrogen and, therefore, by using hydrogen the deactivation can be markedly suppressed and the activity regenerated by hydrogenation of coke, which is impossible with aluminas from Table II. Analogous

TABLE III

Activity of hydrorefining catalysts in the hydrodesulphurization of tetrahydrothiophene in hydrogen at 400°C

Catalyst	<i>k</i> ^a	
	oxide	sulphided
Co-Mo/Al ₂ O ₃ , Cherox 3601	13	76
Co-Mo/Al ₂ O ₃ , Girdler G-35	11	83

^a First order rate constant, mmol g⁻¹ h⁻¹.

situation has been reported by Laine and coworkers²¹ for coke formation from butadiene.

Activity measurements show that the dehydrosulphurization function of hydrorefining Co-Mo/Al₂O₃ catalysts is predominantly connected with the supported phase and not with the alumina support. Dehydrosulphurization activity of alumina alone increases by sulphidation only very little (Table II, this increase was obviously caused by the increased dehydration of the surface during sulphidation), but in the case of hydrorefining catalysts it increased 2 to 3 times (Table I). Dehydrosulphurization was strongly retarded on alumina alone by adding water to the feed, but hydrorefining catalysts were water-insensitive (Fig. 3).

We believe that the mechanism of hydrogen sulphide elimination from tetrahydrothiophene is different for alumina and the supported Co-Mo phase. Interaction of the sulphur of tetrahydrothiophene with alumina is more polar than that with the Co and Mo oxides or sulphides. This results in the former case in that the tetrahydrothiophene molecule is activated preferentially to heterolytic cleavage while in the latter case rather to homolytic cleavage of C—S bond.

In this work, two indirect pieces of evidence were obtained in favour of the assumption that on hydrorefining catalysts the dehydrosulphurization and dehydrogenation of tetrahydrothiophene proceed on the surface site of the same type. The selectivity of dehydrogenation/dehydrosulphurization was constant over broad range of coke formation. Thus, for example, with 1.3 g sample of Co-Mo/Al₂O₃ Cherox 3601(s) catalyst (Fig. 2), the selectivity was followed up to the instant where more than 80 per cent of the sites were blocked by coke formation, this being still constant. The second piece of evidence speaking for the same origin of both reactions is our finding that the activity of hydrorefining catalysts increases 2 to 3 times after pre-sulphidation, but their selectivity is not affected.

Dehydrogenation of tetrahydrothiophene to thiophene results in engaging sulphur electrons in the aromatic ring; the heteroatom in the molecule is masked, the molecule behaves as hydrocarbon and is thus more stable. In this situation, the sulphur cannot interact with the surface such as does in tetrahydrothiophene, and the C-S bond is not activated. The stability of thiophene in the absence of hydrogen on different acid-base and sulphide catalysts is well known (*cf.*²⁴ and for 400°C also *ref.*²⁵). Hence, the reaction of tetrahydrothiophene on hydrorefining catalysts proceeds according to the scheme of two parallel irreversible reactions and the final sulphur-containing products are thiophene and hydrogen sulphide, mutual proportion of which is determined kinetically. The activation energies of both reactions are likely identical, since Hargreaves and Ross¹⁶ observed at the substantially lower temperature 250°C that the selectivity of Co-Mo/Al₂O₃ catalysts is similar with that obtained in the present work, *i.e.* $S = c. 0.6-1.0$.

The essentially complete suppression of dehydrogenation on hydrorefining catalyst after substitution of hydrogen for nitrogen has kinetic reasons, since under out

conditions, the partial equilibrium $T + H_2 \rightleftharpoons THT$ is favourable for thiophene formation (see Fig. 2, thermodynamic data for the calculation are reported in ref.²⁶). The complete suppression of thiophene formation at 250°C by already very low hydrogen pressure (3 kPa) was observed by Hargreaves and Ross¹⁶, while Pazos and coworkers¹⁷ found that dehydrogenation takes place at 290°C even under high hydrogen pressure (2.8 MPa). Thiophene was formed in small amounts in the reaction of tetrahydrothiophene with hydrogen on MoS₂ at 378°C, as reported by Kemball and coworkers²⁷. We have found by thermodynamic calculation that in all the above mentioned cases, the dehydrogenation is limited kinetically.

Hydrogen increases the rate of dehydrosulphurization by more than one order of magnitude (Table III). According to our interpretation, the positive effect of hydrogen manifests itself only in the steps subsequent to the elemental step involving the C—S bond cleavage, this step being identical, irrespective of the presence or absence of hydrogen. Hydrogen accelerates the removal of cleavage products from the surface. The C—S bond cleavage supplies sulphur to the catalyst and the activated hydrogen removes this sulphur and regenerates thus the active sites. The higher rate of desulphidation of the catalyst in hydrogen compared with that in inert gas is well known (*cf.* ref.²⁸). The another product of the cleavage is an unsaturated hydrocarbon fragment — which due to its high unsaturation — desorbs only with difficulty (forming butadiene). In the presence of the activated hydrogen, the fragment is readily hydrogenated to the easier desorbed butenes and butane. We believe that the difficult step here is mainly the removal of the first fragment, *i.e.* sulphur, from the surface since butadiene hydrogenation proceeds even under low hydrogen pressure at faster rate than does the cleavage of tetrahydrothiophene under identical conditions¹⁶.

Comparison of data from Tables I and II shows that the increase in the activity of hydrorefining catalysts after sulphidation is much greater for the reaction in hydrogen than for the reaction in nitrogen. The existence of this phenomenon is now investigated in more detail by us also for other catalysts and its discussion will be presented in another work.

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