THE EFFECT OF HYDROGEN PRESSURE ON DESULPHURIZATION OF DIETHYL SULPHIDE AND THIOPHENE ON A COBALT-MOLYBDENUM CATALYST

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Integral kinetic data for the reaction of diethyl sulphide, thiophene and their mixture have been obtained on a Co-Mo-Al_2O_3 catalyst at 573 K and hydrogen pressures up to 2 MPa. In the reaction of single compounds at low hydrogen pressures and in the reaction of their mixture over the whole range of hydrogen pressures, diethyl sulphide reacts at a faster rate, compared to thiophene. However, both compounds exhibit the same reactivity in their single reactions carried out at hydrogen pressures around 2 MPa. Kinetic behaviour of intermediate products of the above reactions (ethylthiol and tetrahydrothiophene) have been examined. The results obtained lead to the following conclusions: thiophene ring is hydrogenated in the first step of the reaction, the cleavage of the C—S bond in saturated sulphides is an elimination reaction taking place without direct participation of hydrogen, and hydrodesulphurization catalysts are therefore bifunctional.

Thiophene and diethyl sulphide differ significantly in stability during thermal cracking, catalytic cracking in the absence of hydrogen as well as in hydrodesulphurization. In the absence of hydrogen, both aliphatic and alicyclic sulphides undergo thermal decomposition more readily than thiophenes[1]. Oxide and sulphide catalysts decrease markedly the required reaction temperature[2]. Thus, for example, Hargreaves and Ross[3] observed that tetrahydrothiophene decomposes on Co-Mo-Al_2O_3 catalysts in the absence of hydrogen already at 521 K. The decomposition of diethyl sulphide in the absence of hydrogen can be considered as the system of two consecutive reactions (*A*) and (*B*).

$$C_2H_5SC_2H_5 \rightleftharpoons C_2H_5SH + C_2H_4 \tag{A}$$

$$C_2H_5SH \rightleftharpoons C_2H_4 + H_2S \tag{B}$$

Reaction products are unsaturated hydrocarbons which are considerably unstable under reaction conditions. They undergo cracking and condensation reactions. Consequently, the gaseous phase contains also saturated hydrocarbons and hydrogen, and catalyst surface is covered by carbon deposites[2,3]. The presence of hydrogen increases substantially the rate of sulphide decomposition on hydrodesulphurization catalysts. The role of hydrogen is still not quite clear. It seems likely that hydrogen hydrogenates unsaturated hydrocarbons and purifies catalyst surface rather than participates directly in the C—S bond cleavage[2,3]. If this is the case for aliphatic and alicyclic sulphides, then hydrogenolytic cleavage of the C—S bond in hydrodesulphurization of thiophene is even less probable; thiophene sulphur is the part of the aromatic system[4] and the C—S bond is therefore substantially more stable, compared to that bond in saturated sulphides. Hence, in comparison with saturated sulphides thiophene exhibits much greater stability both in thermal[1] and catalytic decomposition in the absence of hydrogen[2]. Similarly to the decomposition of aliphatic sulphides, also the rate of thiophene decomposition is markedly accelerated by hydrogen[2]. It seems that in contradistinction to the reaction of aliphatic sulphides, the main effect of hydrogen on the reaction of thiophene consists in hydrogenation of the aromatic ring (Eq. (*C*)). This is the main reason of the stability of thiophene molecule and the most important hindrance to its further decomposition according to Eqs (*D*) and (*E*).

$$C_4H_4S + 2\,H_2 \rightleftharpoons C_4H_8S \qquad (C)$$

$$C_4H_8S \rightleftharpoons C_4H_6 + H_2S \qquad (D)$$

$$C_4H_6 + 2\,H_2 \rightleftharpoons C_4H_{10} \qquad (E)$$

This was suggested already in the early studies of Moldavsky and Prokopchuk[5] as well as in the works of Cawley and Hall[6]. Decomposition of the saturated intermediate product according to Eq. (*D*) is identical with that according to Eqs (*A*) and (*B*) and hydrogen plays again only indirect role, removing unsaturated products and purifying the catalyst surface.

The above interpretation of hydrodesulphurization of sulphides and thiophenes (which does not involve hydrogenolytic cleavage of the C—S bond) is in accordance with the chemistry of these compounds. Thus, for example, in connection with the principle of microkinetic reversibility it is important that for steps (*A*)–(*E*) also reverse reactions are well known. They are used to describe synthesis of thiophenes from hydrocarbons and hydrogen sulphide on hydrodesulphurization catalysts[7,8]. On the other hand, the reverse reaction to the hydrogenolytic cleavage of the C—S bond of thiophene, *i.e.* Eq. (*F*), seems to be only formal and does not represent a simple chemical transformation. Nevertheless, both alternative mechanisms of hydrodesulphurization of thiophene, *i.e.* direct hydrogenolysis and the reaction course

$$C_4H_6 + H_2S \rightleftharpoons C_4H_4S + 2\,H_2 \qquad (F)$$

according to Eqs (*C*)–(*E*) are still the matter of discussion (*cf.* reviews[9,10]). This dispute is not formal because of its importance for the understanding and optimalization of catalyst function[11]. In an attempt to support the interpretation of hydrodesulphurization of diethyl sulphide based on steps (*A*) and (*B*) and the reaction of thiophene involving steps (*C*)–(*E*), we have compared integral kinetic data at different pressures both for the reaction of single compounds (isolated reactions) and the reaction of their mixture (competitive reactions).

EXPERIMENTAL

Chemicals. Diethyl sulphide and thiophene (Fluka, *purum*) were used as obtained, decaline (Lachema, technical purity grade) was rectified prior to using. Hydrogen (Technoplyn) was deoxygenated on Cherox 40-00 palladium catalyst and dried over a molecular sieve. Cobalt--molybdenum hydrodesulphurization catalyst was commercial sample (G-35, Girdler, Federal Republic Germany).

Apparatus. Experiments were carried out in a pressure tubular flow reactor. The apparatus was described in detail elsewhere[12], except that the i.d. of the reactor was 4 mm, temperature was measured on the external wall of the reactor and hydrogen sulphide formed by the reaction was absorbed in ammoniacal solution of cadmium(II) chloride.

Procedure. Tablets of the catalyst were crushed up and the 0·16—0·25 mm fraction was used. The greater amount of this fraction was reduced and sulphided by $H_2 + H_2S$ mixture at atmospheric pressure. After cooling in nitrogen the catalyst was stored without exclusing the presence of air. The conditions used for sulphidation were reported earlier[13]. Individual catalyst samples used in the reactor were then activated only by heating to the reaction temperature 573 K in hydrogen. Sulphur compounds were fed into the reactor dissolved in decaline (a mixture of the *cis* and *trans* isomer). In experiments with individual compounds the solution contained the sulphur compound and decaline in 1 : 4 mol. ratio, in competitive experiments the thiophene : diethyl sulphide : decaline mol. ratio was 1 : 1 : 3. Liquid components of the reaction mixture were condensated in a cooling trap at 243 K and under the reaction pressure. The condensate was analysed by gas chromatography, using 5% Triton X 305 on Chromosorb W(AW), 3m column, temperature 100°C, hydrogen as a carrier gas, 22 ml (NTP) min^{-1}, a thermal conductivity detector. The amount of hydrogen sulphide absorbed in cadmium(II) chloride solution was determined by iodometric titration. The steady state composition of the reaction products was established fast (to 10 min) and in each experiment it was followed for approx. 1 h (6 samples for analysis). The catalyst was used for several days. The stability of its activity was checked by repeating some runs and the change in its activity during its use did not exceed 15% rel. The results were corrected for this activity decrease. It was verified that decaline is sufficiently stable under conditions of measurements, which was important from the point of view of the chromatographic evaluation.

RESULTS

Integral kinetic data for hydrodesulphurization of diethyl sulphide and thiophene were obtained both for isolated reactions in which the sulphur compounds were injected separately, and for competitive reaction in which a mixture of both compounds was introduced into the reactor.

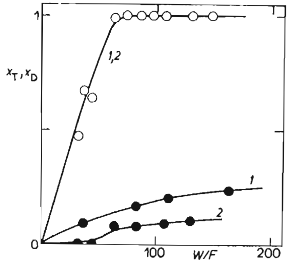
In the first series of experiments, the total pressure P [MPa] in the reactor was atmospheric, initial partial pressures of thiophene, diethyl sulphide and hydrogen, p_T^0, p_D^0 and p_H^0 [MPa] were constant and the variable was the reciprocal space velocity W/F [g h mol^{-1}], where W [g] is the catalyst weight mass and F [mol h^{-1}] is the feed of the sulphur compound. All W/F's are calculated from the feed of only one sulphur compound. The initial partial pressure of decaline p_I^0 in competitive and isolated experiments was not exactly the same. The conversions of thiophene and diethyl sulphide, x_T and x_D, were calculated from chromatographic analyses and are shown for isolated and competitive experiments in Fig. 1. These data were obtained with 0·3 – 1·3 g catalyst samples.

In further experiments, W/F and partial pressures of the sulphur compounds were constant and the variable was hydrogen partial pressure which was changed from

FIG. 1

Integral Kinetic Dependence for Hydrodesulphurization of Thiophene and Diethyl Sulphide at Atmospheric Pressure

$T = 573$ K, $p_{\mathrm{H}}^0 = 0{\cdot}09$ MPa, $P = 0{\cdot}1$ MPa; ● thiophene, ○ diethyl sulphide. 1 Isolated reactions, $p_i^0 = 0{\cdot}002$ MPa (i is T or D), $p_{\mathrm{I}}^0 = 0{\cdot}008$ MPa; 2 competitive system, $p_{\mathrm{T}}^0 = p_{\mathrm{D}}^0 = 0{\cdot}002$ MPa, $p_{\mathrm{I}}^0 = 0{\cdot}006$ MPa.



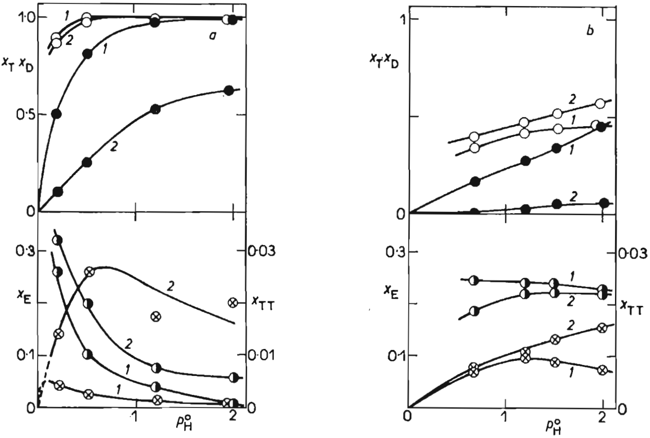


FIG. 2

Hydrodesulphurization of Thiophene and Diethyl Sulphide at 573 K and Different Hydrogen Pressures

a) $W/F = 30$, *b*) $W/F = 5$ g h mol^{-1}. 1 Isolated reactions, $p_i^0 = 0{\cdot}02$ MPa (i is T or D), $p_{\mathrm{I}}^0 = 0{\cdot}08$ MPa; 2 competitive reactions, $p_{\mathrm{T}}^0 = p_{\mathrm{D}}^0 = 0{\cdot}02$ MPa, $p_{\mathrm{I}}^0 = 0{\cdot}06$ MPa. ○ x_{D}, ● x_{T}, ⊗ x_{TT}, ◑ x_{E}.

0·1 to 2·0 MPa. The results for isolated and competitive reactions were obtained for two series with different amounts of the catalyst, *i.e.* on two conversion levels, and are shown in Fig. 2. In these experiments also conversions to the proposed reaction intermediates were followed, *i.e.* the conversion to ethylthiol x_E in the reaction of diethyl sulphide and the conversion to tetrahydrothiophene x_{TT} in the reaction of thiophene. Conversions were calculated from chromatographic analyses and are represented graphically in Fig. 2. In the reaction of diethyl sulphide, tetrahydrothiophene was not detected and the products of the reaction of thiophene did not contain ethylthiol.

Iodometric determination of hydrogen sulphide in the reaction mixture yielded in all cases an independent value of the conversion to hydrogen sulphide x_S. This conversion was calculated also from x_T, x_D, x_E and x_{TT} values obtained from chromatograms and this value was as a rule by 0–15% rel. higher, compared to that obtained by iodometric titration. The recent literature does not report on the more detailed material balance of hydrodesulphurization reaction. The earlier study by Cawley and Hall[6] shows that under higher hydrogen pressures, the composition of sulphur-containing products of the reaction is more complex than it is usually assumed. This fact might explain the defficiency in the amount of the hydrogen sulphide found. In our case this difference in the material balance does not influence the main conclusions of the work.

DISCUSSION

In isolated reaction and under atmospheric hydrogen pressure, diethyl sulphide reacts at a substantially faster rate than does thiophene, as demonstrated by the results shown in Fig. 1. However, as it is seen in Fig. 2, this situation changes with increasing hydrogen pressure. Diethyl sulphide conversion increases with hydrogen pressure only mildly (Fig. 2). This dependence can be explained by assuming that hydrogen is involved only in purification of catalyst surface, as discussed in the introduction. The same indirect influence of hydrogen can be expected also in the reaction of thiophene. However, thiophene conversion increases with hydrogen pressure faster than diethyl sulphide conversion and at hydrogen pressures around 2 MPa the reactivity of both compounds in isolated reactions is the same. It is this more pronounced dependence of the reactivity of thiophene on hydrogen pressure which supports the assumption about the different course of hydrodesulphurization of the aliphatic sulphide and of thiophene. In the reaction of thiophene the greater hydrogen pressure exerts direct effect, *i.e.* it influences the first step of the reaction (that has no analogy in the reaction of the aliphatic sulphide) and accelerates thus the relatively uneasy hydrogenation of the aromatic ring of thiophene (step (*C*)). Example of the marked change in the reactivity of the pair comprising an aliphatic sulphide and thiophene in dependence on hydrogen pressure can also be found in the literature. Thus, for instance, Kieran and Kemball[14] reported that hydrodesulphurization of tetrahydrothiophene on MoS_2 at hydrogen pressures around 0·02 MPa is faster by a factor of ten than the hydrodesulphurization of thiophene. On the other hand, Landa and Mrnková[15] found that on MoS_2 and at a hydrogen pressure of 10 MPa tetrahydrothiophene is significantly more stable compared to thiophene. We believe that if the reaction of both aliphatic sulphide and thiophene were the direct hydrogenolysis of the C—S bond, the rate of both reactions would have been increased analogously, in contradistinction to the experimental finding.

According to the results shown in Fig. 2, on Co–Mo–Al_2O_3 catalyst, at hydrogen pressures around 2 MPa and in isolated reactions, there is not any great difference between reactivity of diethyl sulphide and thiophene. This is not at variance with the industrial experience[8,16] that thiophenes are substantially more stable than aliphatic sulphides under hydrodesulphurization conditions. In industrial hydrodesulphurization sulphur compounds are in mixture, which corresponds to the competitive experiments in this work. Fig. 2 shows that in the competitive system, there exists strong mutual influencing of both compounds and that thiophene is much less reactive than diethyl sulphide even at higher hydrogen pressures. At the same time, the reaction of thiophene is strongly influenced by the pressence of diethyl sulphide but exerts only little effect on the reaction of diethyl sulphide. We believe that the most important role is played here by the competitive adsorption of the starting compounds. One of the possible reasons for a small increase in diethyl sulphide conversion observed for competitive system may be the lower partial pressure of decaline, p_I^0, which compound can compete with the reactants for the catalyst surface.

Also observed kinetic behaviour of the reaction intermediates (ethylthiol and tetrahydrothiophene) can be explained qualitatively in accordance with the mechanism of desulphurization described in the introduction. Forms of dependences of conversions to the intermediate products, x_E and x_{TT}, on hydrogen pressure (Fig. 2) can be interpreted only with difficulty. In this connection it is more advantageous to discuss the dependences $x_E = f(x_D)$ and $x_{TT} = f(x_T)$. In simple case, where the steps (*A*), (*B*) and (*C*), (*D*) would be first order (step (*C*) would be of apparent first order due to excess of hydrogen) the dependence of conversion to the intermediate product x_2 on total conversion of the starting compound x_1 should have the form[17] (*1*):

$$x_2 = \frac{1 - x_1}{K - 1} \left(1 - (1 - x_1)^{K-1}\right) . \qquad (1)$$

The constant K for the reaction of diethyl sulphide can be expressed as $K = k_{(B)} : k_{(A)}$ and for the reaction of thiophene $K = k_{(D)}/(k_{(C)}\,(p_H^0)^n)$ where $k_{(i)}$ is the rate constant for step (*i*) and *n* is the order of the reaction (*C*) in hydrogen. The course of the dependence (*1*) for different *K*'s can be found in literature[17]. It holds that on lowering *K* constant (*i.e.* when the second step of the reaction proceeds at increasingly slower rate compared to that of the first step) the curve for the intermediate product $x_2 = f(x_1)$ shifts to higher x_2 values, *i.e.* in the course of the reaction one can detect higher concentrations of the intermediate product. Under the above assumptions, the dependence (*1*) contains only one constant, is little flexible and does not describe well data for the intermediate products (Fig. 2) which are plotted in coordinates $x_E - x_D$ and $x_{TT} - x_T$. This is not surprising, the kinetics of steps $(A)-(E)$ is clearly more complex than it was assumed in deriving the relation (*1*). For the more complex kinetics of consecutive steps than the first order kinetics, the form of the function $x_2 = f(x_1)$ is impracticable[17]. However, even in our case one can expect the validity of the rule that the faster the first step compared to the second one, the more shifted is the curve $x_2 = f(x_1)$ to greater x_2 values. The curves passing through points in Fig. 3 do not express any particular function $x_2 = f(x_1)$ since one can expect the dependence of the expression $x_2 = f(x_1)$ on p_H^0, and connect thus only points for isolated and competitive reactions respectively.

According to the interpretation discussed in the introduction, both consecutive steps in the hydrodesulphurization of diethyl sulphide are of the same chemical type. These steps are not directly influenced by hydrogen and the change in hydrogen pressure would not affect their relative rates and hence also the curve for the intermediate product, ethylthiol. If hydrogen acts indirectly, as assumed earlier, both steps would be affected analogously. Also parallel hydrodesulphurization of thiophene in the competitive system affects both steps analogously and does not change

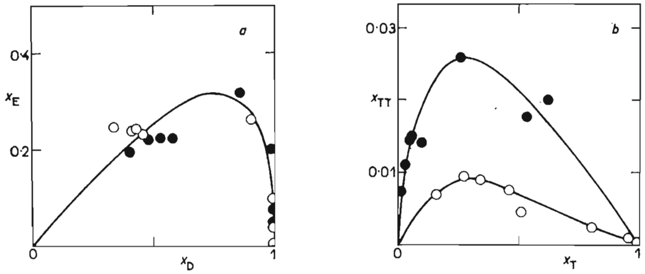


FIG. 3

Kinetic Curves for Intermediate Products of Hydrodesulphurization of Diethyl Sulphide and Thiophene (data taken from Fig. 2)

○ Isolated reactions, ● competitive reactions, *a*) hydrodesulphurization of diethyl sulphide, *b*) hydrodesulphurization of thiophene.

significantly the curve for the intermediate product $x_E = f(x_D)$. In accordance with all these assumptions, points obtained at different hydrogen pressures and for isolated and competitive reactions, shown in Fig. 3, lie roughly on one curve.

Based on the assumptions discussed in the introduction, both consecutive steps in the hydrodesulphurization of thiophene are of different type. The higher hydrogen pressure should enhance the rate of the first step more than that of the second one and should shift the curve $x_{TT} = f(x_T)$ to higher x_{TT} values. This fact is not quite clear from Fig. 3, since experimental x_{TT} values for different hydrogen pressures were obtained at different x_T. Without knowledge of the form of the function $x_{TT} = f(x_T)$, it is difficult to extrapolate these data to the same region of x_T, which is necessary for comparison. However, parallel hydrodesulphurization of diethyl sulphide exerts distinct effect on the relative rate for both consecutive steps in hydrodesulphurization of thiophene. The dependence $x_{TT} = f(x_T)$ in competitive experiments is shifted significantly to higher x_{TT} values, as shown in Fig. 3. Hence, the second step (D) is retarded more than the first one, in which we see the evidence for the different chemical nature of both consecutive steps.

Interpretation of hydrodesulphurization of thiophene in terms of equations $(C)-(D)$ leads to the conclusion that the hydrodesulphurization catalyst acts as the bifunctional catalyst[11]. Both functions, hydrogenation-dehydrogenation (or redox) function and elimination-addition (or acidic) one, depend on hydrogen pressure and temperature in different ways. The ratio of the hydrogenation to elimination activity of the catalyst, indicated by the amount of the intermediate product (tetrahydrothiophene) in the reaction of thiophene increases with increasing hydrogen pressure and decreasing temperature[11]. We believe that the important problem to be further studied is the question what kind of kinetic relation exists between consecutive steps (C) and (D) and what function of the catalyst, hydrogenation or elimination one, limits the overall efficiency of catalyst.

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