

EFFECT OF THE PRETREATMENT CONDITIONS ON THE ACTIVITY OF AN INDUSTRIAL Co-Mo/Al₂O₃ CATALYST

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Received June 15th, 1982

The processes of reduction and sulphidation of an industrial Co-Mo/Al₂O₃ catalyst have been studied by means of gravimetric and kinetic methods at atmospheric pressure. The effect of the pretreatment temperature on the catalytic activity for ethylene hydrogenation and thiophene hydrodesulphurization has been studied. Two types of active centres, for hydrogenation and for hydrodesulphurization, have been characterized on the basis of their different properties.

The effect of the pretreatment conditions on the activity of Co-Mo/Al₂O₃ catalysts has not been thoroughly elucidated. It is known that the catalyst in its oxide form is not active for hydrodesulphurization (HDS), and the data concerning the effect of reduction and sulphidation temperature on catalyst properties are rather contradictory. According to Ripperger and Saum¹, the sulphiding should begin at about 220°C, and the final temperature must not exceed 300°C. The temperature used by de Beer and coworkers² for sulphidation and reduction of the catalyst was 400°C. Hargreaves and Ross³ consider that the optimal catalyst treatment is sulphidation at 300°C and further reduction at 220°C. Beránek and coworkers⁴ investigated the sulphidation of reduced catalysts at temperature 150–450°C and different partial pressures of H₂S up to 40 kPa. Almost all authors have found an enhanced catalytic activity for hydrodesulphurization with increasing the sulphur content in the catalyst during pretreatment^{2,3,5–7}. The majority of papers report a decrease of hydrogenation activity after sulphidation (*e.g.*⁵), though a reverse effect was also observed⁸.

Most authors have found that the isomerization of butenes produced from thiophene decomposition proceeds rapidly. Irrespectively of the conditions of catalyst pretreatment, the contents of individual butenes correspond in all cases to the thermodynamic equilibrium^{3,7}.

Most of the investigations on catalyst composition and reaction mechanism examine the effect of H₂S on the reaction rate. Ramachandran and Massoth⁹ have shown that under fixed conditions of catalyst sulphidation the hydrogenation rate is not affected by the amount of H₂S in the reaction mixture. According to Broderick and coworkers¹⁰, the decrease of catalyst hydrogenation activity in the presence of H₂S is due to structural changes. The same authors have found that an appropriate pretreatment may lead to a structure unaffected by H₂S.

On the other hand, Kolboe and Amberg¹¹ and Fott and Schneider¹² found that H₂S adsorption on a sulphided catalyst or its addition to the reaction mixture caused a substantial decrease of the desulphurization and hydrogenation activity, while the isomerization rate was not

changed. Decrease of rate caused by H_2S formed by the reaction was observed also in the range of higher conversions during thiophene decomposition.

The present paper examines the course of reduction and sulphidation of an industrial Co-Mo/Al₂O₃ catalyst and the effect of sulphidation conditions, especially of the temperature, on hydrogenation and hydrodesulphurization activity of the catalyst.

EXPERIMENTAL

Chemicals. Hydrogen, nitrogen and hydrogen sulphide were of the same origin and purified in the same way as described in previous paper⁴. Ethylene (polymerization grade, Slovnaft, Bratislava) contained no admixtures detectable by gas chromatography and was used without any further purification. Thiophene (Fluka) was used as obtained.

Catalyst. An industrial Co-Mo/Al₂O₃ catalyst containing 11% (wt.) MoO₃ and 3% (wt.) CoO, with a surface area 232 m²/g and average pore radius 2.5 nm was used. The pretreatment of the catalyst (dried at 500°C in nitrogen, 1 h) was carried out in two stages: treatment with H₂ at 400°C and then sulphidation at temperatures ranging from 25 to 425°C with a mixture H₂ : H₂S : N₂ = 1 : 0.13 : 0.2. Both the catalyst activation and catalytic activity tests were performed at atmospheric pressure.

The reduction and sulphiding of the catalyst were measured by a quartz balance⁴ in a flow of H₂ and the sulphiding mixture, respectively. The degree of reduction was measured by following the decrease in catalyst weight owing to the corresponding oxygen removal. The degree of sulphidation was evaluated by the increase in catalyst weight due to the formation of sulphides or other forms of sulphur bound to the catalyst. By heating the sulphided sample for 1 h in a stream of nitrogen, the physically adsorbed sulphur was removed and could be measured by the change in sample weight.

For the measurements of catalytic activity, the catalyst samples were activated at gradientless conditions directly in the catalytic reactor: they were dried at 500°C (60 min) in nitrogen, reduced with hydrogen at 400°C (120 min) and sulphided (150 min) at the required temperature.

Ethylene hydrogenation was carried out in a glass flow reactor at 300°C and a C₂H₄ : H₂ ratio 1 : 1. The details of the apparatus and procedure will be published elsewhere⁸. The reaction mixture leaving the reactor was periodically analyzed for the content of ethane and ethylene by a gas chromatograph with a six-way sampling valve and a flame ionization detector. The column (1 m length) was packed with Porapak Q, temperature 55°C, carrier gas was nitrogen. Following the hydrogenation test (160–240 min), the catalyst was analyzed for sulphur content by the method described in previous paper⁴.

Thiophene hydrodesulphurization was carried out in a flow circulation apparatus at 400°C with a thiophene to hydrogen ratio 1 : 10. The composition of the reaction mixture (thiophene, H₂S, butenes, butane) was determined periodically by a gas chromatograph with a six-way sampling valve and thermal conductivity detector. The conditions of analyses were the same as those described in¹³. The HDS activity was expressed by the rate of thiophene decomposition and the hydrogenation activity by the rate of butane production. The processing of the data was performed by a method given in¹⁴. The standard deviation of rate values of thiophene decomposition and butane production over a stationary catalyst was 0.037 · 10⁻⁶ and 0.4 · 10⁻⁷ respectively (the calculations were made for the catalyst sulphided at 325°C for which the rates of thiophene decomposition and butane production were 3.05 · 10⁻⁶ and 6.72 · 10⁻⁷ mol h⁻¹ m⁻², resp.).

RESULTS

The catalyst reduction at 400°C proceeds at a measurable rate for the first two hours, and is seemingly completed in about 2.5 h (Fig. 1). It should be noted that the reduction ceases when the change in the catalyst weight corresponds to 5–6% of the total weight change for reduction to metallic cobalt and molybdenum. The sulphidation with H₂S of the pretreated catalyst is faster and in about 1 h, irrespectively of the temperature, a steady state is achieved for the given conditions (Fig. 2). The weight changes measured represent 45–55% from the theoretical value calculated for the formation of MoS₂ and CoS from Mo and Co present, and about 80% for the formation of the same sulphides from MoO₂ and Co. About 10% are considered to be physically adsorbed H₂S which can be removed in nitrogen stream (at the same temperature as sulphidation, see Fig. 2). A certain amount of sulphur which is chemically not firmly bound to the catalyst can be removed by hydrogen stream (see also⁴). The estimations of the reduction or sulphidation degrees from weight changes are naturally only approximative since one is not sure whether water formed by reduction or sulphidation was completely removed from the catalyst.

The amount of sulphur remaining after ethylene hydrogenation depends on the temperature of sulphidation. It is increased with the temperature rise, especially above 200°C (Fig. 3). A similar trend in sulphur content was observed for other commercial HDS catalysts after sulphidation and hydrogen treatment at various temperatures⁴.

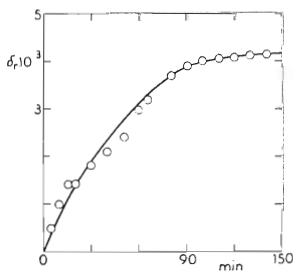


FIG. 1

Relative weight change of the catalyst δ_r as a function of time of hydrogen treatment at 400°C. $\delta_r = (W_d - W_r)/W_r$; W_d weight of catalyst dried in N₂, W_r reduced by H₂

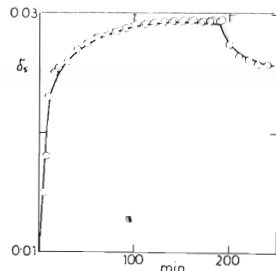


FIG. 2

Relative weight change of the catalyst δ_s as a function of sulphidation time at 325°C. $\delta_s = (W_s - W_r)/W_r$; W_r weight of catalyst reduced in preceding operation, W_s sulphided

The weight percentage of sulphur for 325 and 425°C in Fig. 3 corresponds to a S/Mo atomic ratio of 1.3 and 1.7, resp.

In all cases the sulphided catalyst is more active as compared to the non-sulphided one in ethylene hydrogenation. Its activity is enhanced with rising the sulphidation temperature (Fig. 4) which corresponds to an increase in the amount of chemically firmly bound sulphur (Fig. 3). In Fig. 4, we can observe an initial increase in hydrogenation activity on both curves for sulphided catalysts which can be attributed to a partial removal of sulphur from the catalyst after the sulphiding mixture H_2S/H_2 has been replaced by the C_2H_4/H_2 reaction mixture.

The study on the catalyst HDS activity also reveals an increase with increasing the presulphidation temperature. The same trend is observed for the hydrogenation rate of butenes obtained during the hydrogenolysis of thiophene. A larger relative increase of the hydrogenation activity with the rise of sulphur content in the used catalyst is observed, compared to that of HDS activity (Table I).

On the other hand at the beginning of the reaction, the catalyst continues to bind sulphur removed from thiophene and the measured rate of H_2S formation is considerably lower than the stationary rate. The increase of sulphur in the catalyst and of H_2S on its surface do not cause a variation in the thiophene decomposition rate while that of butane formation is reduced (Fig. 5).

Our measurements have shown that the isomeric mixture of butenes is in a thermodynamic equilibrium. Obviously, isomerization takes place at a considerably high

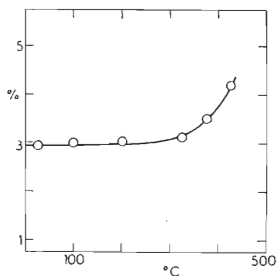


FIG. 3

Dependence of sulphur content (wt. % S) in the catalyst after 4 h of ethylene hydrogenation, on the presulphidation temperature

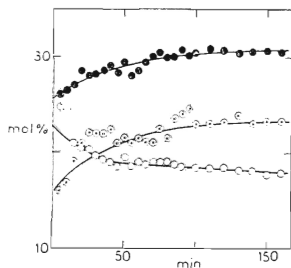


FIG. 4

Conversion to ethane (mol %) vs time of ethylene hydrogenation at 300°C. ○ Without catalyst presulphidation, ⊙ after sulphidation at 25°C, ● after sulphidation at 375°C

rate on the support and the variation in the catalyst composition has no appreciable effect on this reaction.

DISCUSSION

The mere 5–6% reduction of the catalyst observed upon treatment with H₂ shows that in the stage of this pretreatment, Mo⁶⁺ present in the oxide catalyst is only partially reduced. Most probably a mixture of Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺ is obtained as demonstrated by Patterson and coworkers¹⁵ using ESCA.

The sulphidation at the partial pressures of H₂ and H₂S used proceeds at a high rate even at room temperature. The considerable increase of the catalyst hydrogenation activity after sulphidation at 25°C of the reduced sample shows that oxysulphides are very likely present in the catalyst, as assumed in^{16,17} and can be the active species. At this temperature there is little probability of a complete substitution of oxygen

TABLE I

Effect of the presulphidation temperature on the rate of thiophene decomposition (R_t) and butane production (R_b) in mol/h m². T_r temperature of catalyst reduction by hydrogen, T_s presulphidation temperature of catalyst, S (wt.%) amount of sulphur remaining in the catalyst

T_r , °C	T_s , °C	S , %	$R_t \cdot 10^6$	$R_b \cdot 10^6$
400	325	3.2	3.0	0.67
400	375	3.5	3.4	0.82
400	425	4.2	3.6	1.00

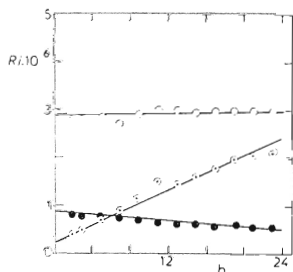


FIG. 5

Reaction rate R_i at 400°C (mol/h m²) vs time of reaction after catalyst presulphidation at 325°C. ○ Thiophene decomposition, ⊙ production of H₂S, ● production of butane

attached to cobalt and molybdenum. This assumption is supported by the fact that the degree of sulphidation to MoS_2 and CoS even at 425°C is not higher than 70%.

The dependence of the amount of sulphur in the catalyst on time and sulphidation temperature is analogous to that observed by de Beer and coworkers². The marked increase of hydrogenation activity upon sulphidation, even at 25°C , can be explained in two ways: *a*) either hydrogenation proceeds with a considerably higher rate on sulphided centres, or *b*) the reduction of Mo^{6+} to the lower valency state, active in hydrogenation, proceeds much easier in the presence of H_2S or sulphur anions substituted for oxygen in the original form of the catalyst, than the reduction of this oxidic form by hydrogen alone which is rather a slow process (see also^{8,18}).

According to Desikan and Amberg¹⁹, the amount of reversibly adsorbed sulphur will exert an inhibitory effect on the catalyst activity. On the other hand, the chemically firmly bound sulphur, causing a change in the catalyst composition, plays important role for its activity. A part of it (less firmly bound) can be removed, at the temperatures used, by interaction with hydrogen^{4,8,12,20} in the absence of H_2S or other sulphur compounds, giving rise to anionic vacancies which can act as additional catalytic centres. This might be the reason of increasing hydrogenation activity in the initial period of ethylene reaction on freshly sulphided catalyst (Fig. 4).

The binding of H_2S resulting from thiophene decomposition in addition to the catalyst presulphidation with H_2S causes no further change in HDS activity. This is indicative of a stable structure formed during the catalyst activation under the above conditions. However, the hydrogenation activity is slightly lowered (Fig. 5).

Thus, the different effect of sulphur on catalyst activity for hydrogenation and HDS suggests the occurrence of two types of active centres. The experimental observations leading to this view can be summarized in the following way: *a*) The increase of activity with increasing amount of chemically bound sulphur is more pronounced for hydrogenation than for hydrodesulphurization (Table I); *b*) HDS activity is not affected by H_2S resulting from thiophene decomposition, whereas hydrogenation activity is reduced (Fig. 5); *c*) hydrogenation activity is increased by removal of a part of less firmly bound sulphur in hydrogen atmosphere (Fig. 4).

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Translated by the author (L. B.).