
RELATION BETWEEN REDUCTION AND SULPHIDATION PROCESS DURING THE ACTIVATION OF A Co-Mo/Al₂O₃ HYDRODESULPHURIZATION CATALYST*

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The course of activation at 673 and 773 K of an industrial hydrodesulphurization catalyst CHEROX 36-01 was followed gravimetrically. Reduction with hydrogen, reductive sulphidation with a H₂S/H₂ mixture, non-reductive sulphidation with a H₂S/He mixture and sulphidation of prerduced catalysts were compared. All sulphidation procedures are much faster than the reduction alone, the latter has, however, a higher apparent activation energy. In the reductive sulphidation with H₂S/H₂, reduction and sulphidation take place simultaneously, sulphidation being a predominant process at the beginning of the activation, especially at 673 K. It has been shown how the two processes can be decoupled or superposed. The catalytic activity in ethylene hydrogenation develops much more slowly when the catalyst is activated only by reduction than when it is activated by reductive sulphidation, in accordance with the relative velocities of these two activation procedures. The hydrogenation activity of catalysts reduced to a different extent correlates with their oxygen chemisorption capacity at 195 K.

The cobalt-molybdenum hydrorefining catalysts, supplied in the form of oxides supported on alumina, become active for the reactions involved in the hydrorefining process only after treatment with hydrogen or, more frequently, with hydrogen and a sulphur containing compound. Several variations of the activation procedure may be used, such as activation by the sulphur compounds contained in, or added to, the feedstock itself during the first period of the hydrorefining process, or activation by presulphiding the catalyst before the process with a mixture of hydrogen and a simple sulphur containing molecule (*e.g.* H₂S, CS₂). Presulphiding in wet phase, *i.e.* by soaking the catalyst with a nonspiked or spiked feedstock (containing *e.g.* dimethyl sulphide or dimethyl disulphide) and then increasing the temperature to a value at which the sulphur compound is decomposed is also possible¹. One of the most widely used procedures is the presulphiding in gas phase with a H₂S/H₂ mixture. During presulphiding, two main chemical processes take place in competition: *a)* reduction of the Mo and Co oxides to lower valency states and *b)* sulphidation of the oxides, *i.e.* replacement of oxygen with sulphur. In preceding papers^{2,3}, we studied the sulphidation with H₂S/H₂ of prerduced Co-Mo catalysts, *i.e.* we separated the sulphidation from the reduction and established the effect of H₂S partial pressure and temperature on the kinetics and the final degree of sulphidation.

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In the present paper we studied the velocity of various gas-phase activation procedures of a commercial Co-Mo/Al₂O₃ catalyst in oxidic form, namely its reduction with hydrogen, its sulphidation at non-reductive conditions and its reductive sulphidation. The aim of the study was to compare the relative rates of reduction and sulphidation processes involved in the activation and their temperature dependence, and to analyze how the two processes are superposed when they take place simultaneously during the reductive sulphidation with a H₂S/H₂ mixture. The results were compared with the sulphidation of prereduced samples and with the velocity of development of the catalytic activity in the ethylene hydrogenation during the various activation procedures. Additional measurements of the oxygen chemisorption ability of catalyst samples reduced to a different extent could provide information on the relation between the catalytic hydrogenation activity and the surface concentration of molybdenum in lower valency state during the activation.

EXPERIMENTAL

Chemicals. Hydrogen, nitrogen and hydrogen sulphide were of the same origin and purified in the same way as described in previous paper². Oxygen (Technoplyn, Prague) was dried with the molecular sieve CALSIT 5. Ethylene (Chemical Works Litvínov, Czechoslovakia, purity 99.8%) was used directly from the pressure cylinder. Helium (Messer Griesheim, Austria, 99.996%) was purified and dried in the same way as nitrogen².

Catalyst. Commercial HDS catalyst CHEROX 36-01 (Chemical Works Litvínov, Czechoslovakia) contained 14.1 wt.% MoO₃ and 3.55 wt.% CoO. Its specific surface area was 222 m² g⁻¹, most frequent pore radius 2.5 nm. The pellets were crushed, sieved and the fraction 0.16–0.315 mm was used.

Gravimetric measurements. Weight changes in dependence on time were measured during reduction and/or sulphidation of the catalyst with a quartz balance in a flow of corresponding gases by a procedure described in detail in². With a dry catalyst (calcined 1 h at 773 K in a flow of dry nitrogen) following runs were performed: a) reduction with hydrogen at 673 K and 773 K; b) sulphidation with a H₂S/He mixture at 773 K [$p(\text{H}_2\text{S}) = 5.1$ and 10.0 kPa, resp.] and at 673 K [$p(\text{H}_2\text{S}) = 5.1$ kPa]; c) sulphidation with a H₂S/hydrogen mixture at 773 K [$p(\text{H}_2\text{S}) = 1.0$; 5.1 ; 10.0 ; 20.3 kPa, resp.] and at 673 K [$p(\text{H}_2\text{S}) = 5.1$ and 10.2 kPa]; d) sulphidation with a H₂S/hydrogen mixture at 773 K [$p(\text{H}_2\text{S}) = 5.1$ kPa] after pre-reduction of the catalyst with hydrogen at the same temperature for 60, 120, 240 and 420 min, resp. The results are expressed as relative weight change δ_r (%) calculated from the difference between the initial weight of dry sample w_0 and its weight w_t at reaction time t

$$\delta_r = (w_t - w_0)/w_0 \quad (1)$$

Tests of catalytic activity and oxygen chemisorption measurements on samples activated by reduction alone were performed in a combined flow apparatus working at atmospheric pressure and equipped with a FID detector for chromatographic analysis of reaction products (Porapak Q, 328 K) of ethylene hydrogenation and with a thermal conductivity cell for detection of oxygen uptake. In this apparatus, activation, ethylene hydrogenation and/or oxygen chemisorption were carried out on the same catalyst sample without its transfer. The details of the apparatus are described elsewhere^{4,5}. Dry catalyst samples (1 h at 773 K in nitrogen) were activated with

a flow of hydrogen for 1–7 h at 773 K and then ethylene hydrogenation at 573 K was carried out (H₂/C₂H₄ molar ratio 1 : 1) and reaction products were periodically analyzed until a steady conversion was achieved (aprox. after 75 min). After the reaction, the catalyst was flushed with hydrogen at 573 K for additional 30 min, then heated in a flow of helium to 773 K, kept at this temperature for 1 h, cooled to 195 K, kept at this temperature for 1 h (still in a flow of helium) and then, at the same temperature, pulses of oxygen (0.22 ml) were periodically introduced into the helium flow. The oxygen uptake was registered until its peaks in the exit flow reached a constant height. In some experiments, the activity tests (on samples activated with hydrogen at 673 and 773 K, resp.) and chemisorption measurements were performed separately. In separate chemisorption measurements, the catalyst activated with hydrogen at 773 K was flushed with helium at the same temperature for 1 h and then treated as described above.

With sulphided samples, only catalytic activity was measured at the same conditions as above in a separate common catalytic flow reactor. Before the activity tests, the catalyst samples were activated for 1–12 h directly in the reactor at 773 K with a H₂S/H₂ 1 : 9 mixture either immediately after drying at 773 K (nitrogen, 1 h) or after drying and 4 h prerreduction with hydrogen at 773 K. With sulphided samples, the time necessary to achieve a steady ethylene conversion was longer (about 2–4 h) than with reduced samples. In both cases, the steady conversion values were taken as a measure of catalytic activity in further discussion.

RESULTS AND DISCUSSION

Gravimetric Study of Catalyst Activation

Weight changes of catalyst containing oxides of Mo and Co caused by reduction are negative (loss of oxygen in the form of water) and those caused by sulphidation are positive (replacement of oxygen by heavier sulphur). Time dependencies of relative weight changes monitored gravimetrically during reduction with hydrogen, sulphidation with H₂S in an inert medium (helium) and reductive sulphidation with H₂S in hydrogen, resp., all at 773 K, are plotted in Fig. 1. The shape of the curve 1 indicates that reduction is a rather slow process which, even after 420 min, does not achieve a steady state. The velocity of weight changes in the sulphidation with H₂S/He is much higher (curve 2) and a steady state is achieved after 20–30 min. Comparison with analogous experiments performed at 673 K (curves 1 and 2 in Fig. 2) allows us to estimate the difference in temperature dependence of the two processes. The difference is seen also in Table I, where the values of initial rates of reduction and sulphidation at 673 and 773 K, resp., are given (calculated as slopes in the origin of the respective curves in Figs 1 and 2). At 673 K, sulphidation proceeds about 25 times faster than reduction while at 773 K it is only about 3 times faster. The values in Table I indicate that the apparent activation energy of reduction is higher than that of sulphidation.

The curves 3–6 in Fig. 1 represent the results of reductive sulphidation with a mixture of hydrogen sulphide and hydrogen. In this case, both reduction and sulphidation take place simultaneously and the resulting weight changes are given by their superposition. This superposition of fast sulphidation and slow reduction results

in the appearance of maxima at the very beginning of the activation (rapid increase of weight by sulphidation) followed by a slow decrease (due to reduction) of δ_r to a steady value. Both the velocity and the extent of sulphidation manifested by the height of maximum and by the steady δ_r value depend on the H_2S partial pressure, in agreement with our previous results with prerduced catalyst². It is worth noting,

TABLE I

Comparison of initial rates of reduction with hydrogen (r_r^0) and of non-reductive sulphidation (r_s^0) with a $\text{H}_2\text{S}/\text{He}$ mixture [$p(\text{H}_2\text{S}) = 5.1 \text{ kPa}$]

| Initial rates $r_i^0 \cdot 10^3, \text{ s}^{-1}$ | 673 K | 773 K |
|---|---------|-------|
| | r_s^0 | 3.3 |
| r_r^0 | 0.13 | 1.3 |

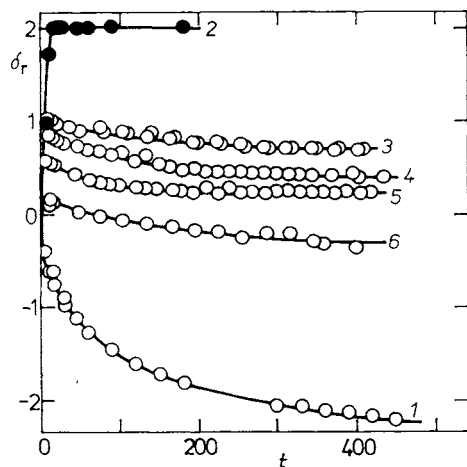


FIG. 1

Dependence of relative weight changes δ_r (%) of catalyst samples reduced and/or sulphidated at 773 K on the time of activation t (min). 1 Reduction with H_2 ; 2 sulphidation with a $\text{H}_2\text{S}/\text{He}$ mixture, $p(\text{H}_2\text{S}) = 5.1 \text{ kPa}$; 3–6 sulphidation with a $\text{H}_2\text{S}/\text{H}_2$ mixture: 3 $p(\text{H}_2\text{S}) = 20.3 \text{ kPa}$; 4 $p(\text{H}_2\text{S}) = 10.0 \text{ kPa}$; 5 $p(\text{H}_2\text{S}) = 5.1 \text{ kPa}$; 6 $p(\text{H}_2\text{S}) = 1.0 \text{ kPa}$

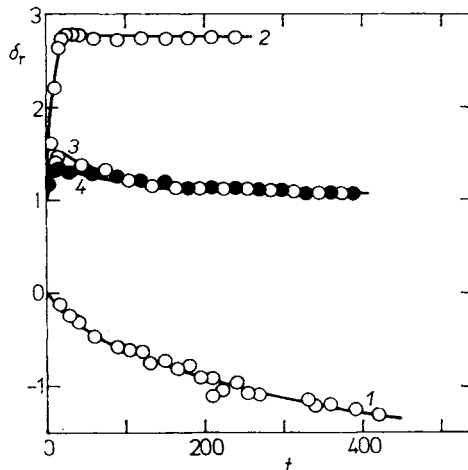


FIG. 2

Dependence of relative weight changes δ_r (%) of catalyst samples reduced and/or sulphidated at 673 K on the time of activation t (min). 1 Reduction with H_2 ; 2 sulphidation with a $\text{H}_2\text{S}/\text{He}$ mixture, $p(\text{H}_2\text{S}) = 5.1 \text{ kPa}$; 3, 4 sulphidation with a $\text{H}_2\text{S}/\text{H}_2$ mixture: 3 $p(\text{H}_2\text{S}) = 10.2 \text{ kPa}$, 4 $p(\text{H}_2\text{S}) = 5.1 \text{ kPa}$

however, that not only the initial velocity of weight changes is higher, but also the steady state is achieved sooner by reductive sulphidation than by reduction with hydrogen only. The steady state is achieved the sooner the higher is the H₂S partial pressure. This leads to the suggestion that the reduction process is promoted by the presence of hydrogen sulphide (or another form of sulphur on the catalyst surface), which is fully in line with the results of the study of temperature programmed reduction and sulphidation⁵ and with the fact to be discussed later in this paper, namely that the development of catalytic hydrogenation activity by reductive sulphidation is much faster than by reduction with hydrogen only.

From the values of initial rates listed in Table I one may assume that at lower temperature (673 K) the relative contribution of sulphidation at the beginning of the coupled process will be even larger than at 773 K. Evidently, at 673 K, larger values of δ_r with flatter maxima (curves 3 and 4 in Fig. 2) than at 773 K (curves 4 and 5 in Fig. 1) and slower decrease of δ_r after these maxima are due to markedly higher ratio r_s^0/r_r^0 at 673 K. These results, too, seem to support the above mentioned assumption of superposition of reduction and sulphidation during the reductive sulphidation with a H₂S/H₂ mixture. Though the curves could not be simulated by a simple mathematical superposition (the two reactions are probably not fully independent, it seems *e.g.* that reduction is promoted by H₂S – see preceding paragraph), the results suggest that the course of reductive sulphidation is reasonably predictable from the data for the two isolated reactions.

To provide additional evidence for the above assumption we tried to decouple the two processes by postponing the start of sulphidation after the sample had been prerduced to different extent. The results of sulphidation with H₂S/H₂ mixture starting after 60, 120, 240 and 420 min, resp., of prerduction are shown in Fig. 3. Sulphidation of prerduced samples was very fast. The initial velocity of weight increase did not change for prerduction times longer than 1 h and was estimated to be about $4.5 \cdot 10^{-3} \text{ s}^{-1}$. As the reduction had been partially accomplished before the H₂S/H₂ mixture was introduced, its contribution to the resulting weight change in the coupled process diminishes with the time of prerduction; this is demonstrated by suppression of maxima on the curves in Fig. 3 at longer prerduction times.

Catalytic Activity and Oxygen Chemisorption

In addition to gravimetric measurements we have investigated also the development of catalytic activity with time in three different activation procedures and, with reduced samples, also the development of oxygen chemisorption capacity. The results are an extension of those already published⁶. The dependence of ethylene conversion in hydrogenation reaction on the time of activation is demonstrated in Fig. 4. It can be seen that with catalyst samples activated at 773 K by any of the three procedures, about the same value of ethylene conversion (0.36–0.38) is achieved.

It is also apparent, however, that with catalysts activated directly with a $\text{H}_2\text{S}/\text{H}_2$ mixture (curve 3) the mentioned conversion value is approached much faster than with catalysts reduced only by hydrogen (curve 1) or with catalysts prerduced and then sulphided (curve 1a). The development of catalytic activity by reduction of the catalysts at lower temperature (673 K, curve 2) is very slow which contrasts with a much higher conversion (0.24) obtained after 4 h of sulphidation with a $\text{H}_2\text{S}/\text{H}_2$ mixture at the same temperature.

The fact that at sufficiently high temperature all the activation procedures lead (with different velocity, however) to an approximately equal activity indicate that in ethylene hydrogenation, the active sites may be the same, irrespective of the activation procedure used. Then, the role of hydrogen sulphide or any other form of sulphur in creating hydrogenation active sites on the surface of $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalyst may consist only in accelerating the process of molybdenum reduction, as already mentioned.

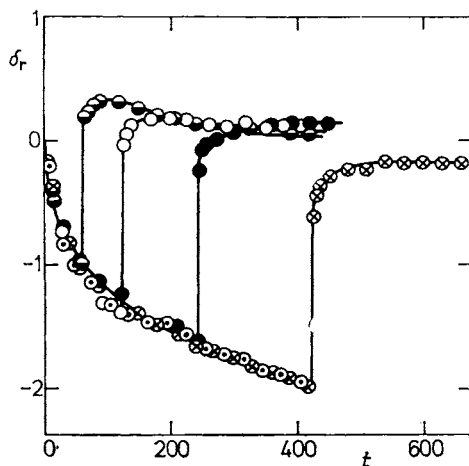


FIG. 3

Dependence of relative weight changes δ_r (%) on the time of activation t (min) for catalyst samples prerduced with H_2 and then sulphided with a $\text{H}_2\text{S}/\text{H}_2$ mixture [$p(\text{H}_2\text{S}) = 5.1$ kPa], both at 773 K. Pre-reduction: ● 60 min; ○ 120 min; ● 240 min; ⊕ 420 min. For comparison: ⊙ only reduction with hydrogen without following sulphidation

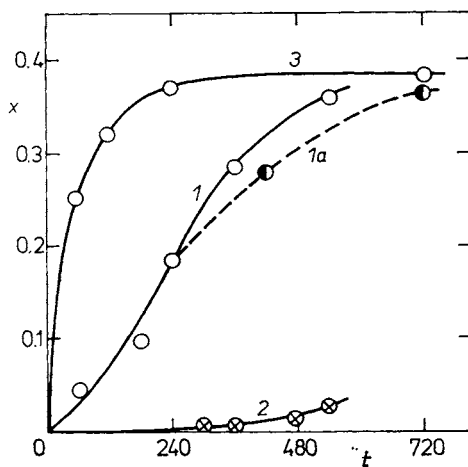


FIG. 4

Dependence of the extent of conversion x in ethylene hydrogenation (ethylene space velocity $335 \text{ mol h}^{-1} \text{ kg}^{-1}$) on the time t (min) of catalyst activation. 1 Reduction of catalyst with H_2 at 773 K; 1a after 240 min of pre-reduction at 773 K the catalyst was sulphided with a $\text{H}_2\text{S}/\text{H}_2$ mixture [$p(\text{H}_2\text{S}) = 10.0$ kPa] at the same temperature; 2 reduction with H_2 at 673 K; 3 reductive sulphidation at 773 K with a $\text{H}_2\text{S}/\text{H}_2$ mixture [$p(\text{H}_2\text{S}) = 10.0$ kPa]

In Fig. 5, the dependencies of catalyst weight change during activation and of catalytic activity tested by ethylene hydrogenation on the time of activation by reduction with H₂ are compared. The parallel course of both curves indicates that catalytic hydrogenation activity is proportional to the extent of catalyst reduction. A curve very similar to curve 2 in Fig. 5 was also obtained⁷ for hydrogenation of cyclohexene at 593 K.

Specific oxygen chemisorption at low temperature is thought to be a measure of the amount of molybdenum in lower valency state on the surface of hydrodesulphurization catalysts. Although variant views on detailed nature of specific chemisorption sites can be found in the literature (suggestions ranging from Mo⁴⁺ to Mo²⁺ cations or possibly anion vacancies connected with them⁸⁻¹¹), the opinion that these sites are created in the process of reduction of molybdenum surface species is generally accepted. In Fig. 6, correlations are shown between catalytic activity (expressed as apparent 1. order rate constant of ethylene hydrogenation) and oxygen

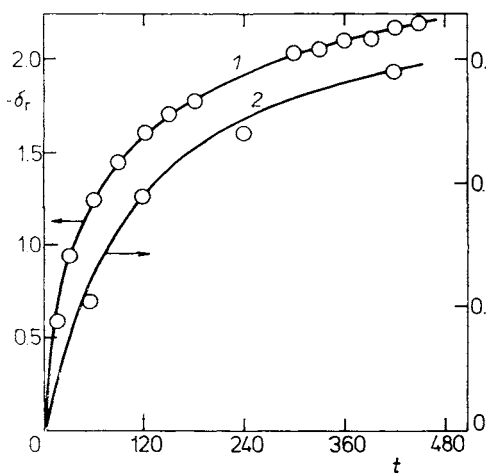


FIG. 5

Dependencies of relative weight change δ_r (%) 1 and of ethylene conversion x 2 on the time of activation t (min). Catalyst was activated by reduction with hydrogen at 773 K, hydrogenation reaction performed at 573 K and ethylene space velocity 130 mol h⁻¹ kg⁻¹

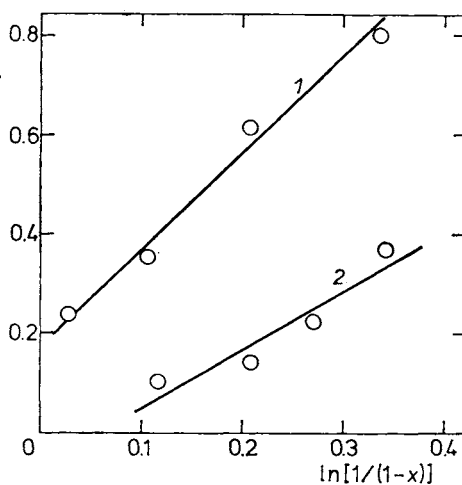


FIG. 6

Correlations of the apparent 1. order rate constant expressed as $\ln[1/(1-x)]$ of ethylene hydrogenation at 573 K with the volume V (ml g⁻¹) of oxygen chemisorbed on freshly reduced catalyst (curve 1) and on the catalyst after the hydrogenation reaction (curve 2). Catalyst samples were reduced with hydrogen at 773 K to different extent, oxygen volume V was measured at 293 K and 100 kPa

chemisorption capacity of catalysts reduced to different extent. Approximate linear dependencies were obtained both for chemisorption measured on catalysts immediately after reduction and for that measured on reduced catalysts after the hydrogenation test reaction. Oxygen chemisorption capacity of freshly reduced catalysts was larger (curve 1) than the capacity of catalysts used in the catalytic reaction (curve 2). In our catalytic experiments the ethylene conversion also decreased during the reaction, *i.e.* a drop was observed from the initial value on fresh catalyst to the steady value attained approx. after 75 min of catalytic reaction. A similar decrease of oxygen chemisorption capacity before and after the reaction was found¹² also for unsupported MoS₂, but no decrease of dibenzothiophene conversion was observed in the catalytic HDS reaction used. Though this variance may be caused by the difference in catalyst activation procedure and test reaction used, the fundamental facts are to be put forward (*a*) that there is no reason to assume identical active sites for hydrogenation and HDS reaction and (*b*) that there is no clear evidence till now for identity of any kind of these sites with the sites active in oxygen chemisorption.

In the case of ethylene hydrogenation, the results shown in Figs 5 and 6 reveal that for reduced Co-Mo/Al₂O₃ catalyst, the hydrogenation activity is proportional both to the extent of bulk reduction and to the amount of chemisorbed oxygen. Thus, our results can be interpreted as a further support of the opinion^{8,9} that catalytic activity in hydrogenation on HDS catalysts is associated with molybdenum in reduced form. Our results suggest that even in sulphided catalysts, the activity in olefin hydrogenation is probably connected only with molybdenum and that the reduction of the original oxidic form of molybdenum to the active one proceeds much faster in the presence of hydrogen sulphide or any other form of sulphur (*e.g.* anions S²⁻) on the catalyst surface than in the presence only of hydrogen. The role of sulphur in other reactions involved in HDS process is, however, more complex. The behaviour of sulphided catalysts in hydrogenation and in other reactions involving isomerization and C-S and C-C bond splitting as well as the activity *vs* oxygen chemisorption correlations are being investigated in our laboratory⁷ as a continuation of the present paper.

LIST OF SYMBOLS

| | |
|-------------------------|---|
| $p(\text{H}_2\text{S})$ | partial pressure of hydrogen sulphide (kPa) |
| r_r^0, r_s^0 | initial rates of catalyst reduction and sulphidation, resp. (10^3 s^{-1}) |
| t | time of catalyst activation (min) |
| V | volume of chemisorbed oxygen (ml g^{-1} , measured at 293 K and 100 kPa) |
| w_0, w_t | weight (g) of dry catalyst sample and its weight after activation time t , resp. |
| x | extent of conversion in ethylene hydrogenation to ethane |
| δ_t | relative weight change (%) calculated according to Eq. (1) |

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