CHEMISORPTION OF OXYGEN AND HYDROGENATION OF ETHYLENE ON SULPHIDED Co–Mo/Al₂O₃ CATALYST. EFFECT OF ACTIVATION PROCESS

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Oxygen chemisorption by pulse dynamic method at room temperature and the activity for ethylene hydrogenation at 300°C in a flow regime were determined for Co–Mo/Al₂O₃ catalyst CHEROX 36-01 sulphided by a $H_2S/H_2(1 : 10)$ mixture at 400°C. The measurements were carried out either immediately after sulphidation or after subsequent reduction of the sulphided catalyst by hydrogen. The chemisorption of oxygen was measured both prior to and after the catalytic reaction. In addition, the reactivation of the catalyst was examined after its passivation by oxygen chemisorption. The reactivation was effected either by resulphidation or by reduction with hydrogen at 400°C, on repeated reactivation also by combination of both procedures, variables being the time of activation and reactivation steps. The results are discussed from the standpoint of the structure and interrelation between active sites for oxygen chemisorption and catalytic, especially hydrogenation reactions. Formation of coordinately unsaturated sites and SH groups is emphasized. The reasons of possible failures in correlations between chemisorption capacity for oxygen and catalytic activity are mentioned.

Oxygen chemisorption has been often used for characterization of hydrodesulphurization catalysts. The utilization of this information and the possibility of deduction of general conclusions from the results obtained by this method are however impeded by a great variety of the catalysts studied and of the methods used in their pretreatment in different laboratories. While differences found in chemisorption measurements with the reduced oxide[1,2] and sulphide[3] catalysts are accounted for by the difference in atomic volume of molybdenum bonded in MnO_2 and MoS_2, the higher chemisorption capacity of the sulphided-reduced MoS_2 (ref.[3]) compared to the MoS_2 activated only by sulphidation[4,5] is attributed by Fierro and coworkers[3] unambiguously to the different procedures of catalyst pretreatment. The above authors compared[3] also the chemisorption capacity of the sulphided and reduced forms of Mo/Al_2O_3 catalyst (both obtained by activation at 450°C) and found that the capacity of the reduced form was substantially higher. The authors believe that this phenomenon results either from the difference in dispersion of MoO_2 and MoS_2 on the support surface or from the plugging of support pores in the presence of bulkier MoS_2 molecules. Our experience[6,7] with the reduced and sulphided Co–Mo/Al₂O₃ catalyst shows that the sulphided form exhibits greater tendency to sintering at higher temperatures. The decrease of chemisorption capacity of the sulphided Co–Mo/Al₂O₃ catalyst by sintering at high activation temperatures was reported also by Prada Silvy and coworkers[8]. Another study of the effect of the activation process on chemisorption of oxygen with one MoS_2 catalyst was presented by Kalthod and Weller[9] who examined also the activity of catalyst in hydrogena-

tion of propylene. The activation was carried out in temperature-programmed regime. After sulphidation with a hydrogen–hydrogen sulphide mixture, chemisorption was significantly lower than after activation with hydrogen only. When hydrogen was applied after the sulphidation mixture, the chemisorption acquired again the value obtained after direct activation by hydrogen. The activity of the catalyst in hydrogenation reaction was sensitive to the activation procedure, however, it did not correlate with chemisorption capacity. It was found that different activation procedures result in considerable changes in the structure and properties of the surface of the catalyst.

In our previous work[6] we reported on the measurements of oxygen chemisorption on the reduced Co–Mo/Al$_2$O$_3$ catalyst in the freshly activated or working state. The model reaction was hydrogenation of ethylene. The chemisorption capacity of the catalyst after the hydrogenation reaction was markedly lower than immediately after the reduction. Similarly, the ethylene conversion acquired maximum value at the beginning of the reaction and then decreased to a steady value. However, in a study of MoS$_2$ catalyst[4] where hydrodesulphuration of dibenzothiophene was used as model reaction, the chemisorption capacity after the reaction and resulphidation was lower than that of the freshly activated catalyst although the activity decrease during the reaction has not been observed. Another work[10] dealing with MoS$_2$ catalyst in CO hydrogenation showed again that the chemisorption capacity is lower after the reaction compared to the freshly sulphided catalyst. Catalytic activity decreased during the reaction, similarly as in the study by Zahradníková and coworkers[6]. Both values of the chemisorption capacity were, however, obtained during one experiment, using the sequence of steps: sulphidation — chemisorption — resulphidation — — reaction — resulphidation — chemisorption. Kalthod and Weller[9] found that resulphidation of MoS$_2$ decreases chemisorption capacity. Bodrero and Bartholomew[5] then found that an insufficient purification of the pure MoS$_2$ from H$_2$S or reaction products, which could have occured also in the pretreatment procedure chosen by Tauster and collaborators[4], always decreases chemisorption capacity (in contradistinction to the supported sulphided catalysts in which case the reverse situation has been encountered). We consider it likely that for the catalysts and reactions studied in other works, different procedure of the catalyst activation would lead to the different ratios of both chemisorption capacities.

The activation process as well as oxygen chemisorption on HDS catalysts have been studied in our laboratory. We investigated first the activation by hydrogen of the Co–Mo/Al$_2$O$_3$ catalyst and correlated oxygen chemisorption with activity in hydrogenation of ethylene both for the freshly reduced catalyst and for the catalyst in working state[6]. Then we worked out the method of chemisorption measurements on the sulphided catalyst, and examined the effect of temperature and time of sulphidation[11]. Finally, in the recent work[7] we have paid detailed attention to the effect of the other steps of the pretreatment process as well as to the obtainable accuracy and reproducibility of the results.

In the present work we were concerned with the effect of the activation process on the chemisorption capacity and catalytic activity in ethylene hydrogenation of the sulphided Co–Mo/Al$_2$O$_3$ catalyst. We were also interested in chemisorption capacities on the reactivated surface and on the surface in working state. We worked with one catalyst, excluding the effect of other conditions of pretreatment procedure as completely as possible. Our aim was to contribute to the elucidation of the effect of the activation process and hydrogenation reaction on oxygen chemisorption in the

case of sulphided catalysts, to improve recent ideas about the appropriate arrangement of the experiment when characterizing these catalysts by oxygen chemisorption, and in view of both the earlier and new information to attempt to provide a more realistic evaluation of possibilities and/or limitations of oxygen chemisorption as the method for characterization of HDS catalysts.

EXPERIMENTAL

Chemicals. Hydrogen, hydrogen sulphide, ethylene, oxygen and helium. Their origin and treatment were described previously[6,7].

Catalyst. Czechoslovak commercial Co–Mo/Al₂O₃ catalyst CHEROX 36-01 (Chemical Works Litvínov, Czechoslovakia); 14·1 wt. % MoO_3, 3·55 wt. % CoO. Its properties and treatment were described earlier[6,7].

Apparatus and procedure. Chemisorption of oxygen was measured by pulse dynamic method at room temperature, using the apparatus described in detail in our previous paper[7]. The same apparatus was used to test the catalytic activity in the hydrogenation of ethylene. The apparatus was constructed to enable activation, catalytic and chemisorption measurements in the same reactor, without manipulation with the catalyst. Standard procedure of chemisorption measurement was as follows: A sample of catalyst was warmed up in a stream of helium in 15 min to 400°C, dried at this temperature under helium for 1 h and then sulphided with a hydrogen––hydrogen sulphide mixture (10 : 1). After the sulphidation, the catalyst was flushed with helium at 400°C for 1 h, cooled and then maintained at room temperature (20–25°C) for 1 h. At this temperature oxygen chemisorption was measured.

In the standard test of catalytic activity, a sample of the catalyst was activated similarly as prior to the chemisorption measurement; however, during last 5 min of the activation, temperature was decreased to 300°C and a mixture of hydrogen and ethylene (1 : 1) was introduced into the reactor. The first analysis of the reaction products was done after 15 min, the second after 30 min and then after every 30 min for a total period of 4·5 h, in one control experiment for 9 h. The ethylene conversion ceased to increase after 3·5 h to 4·5 h. In one case, after 1 h-sulphidation at 400°C, the catalyst was first flushed with helium at 400°C for 1 h as prior to the chemisorption measurement and only then the temperature was adjusted to 300°C and the reaction performed on the purified surface. The course of conversion increase and its steady value did not differ from the measurements carried out immediately after the activation. The activity of the catalyst was characterized by the molar fraction of ethane in the ethane-ethylene mixture at steady conversion, which value was determined from the heights of chromatographic peaks, using the calibration curve.

Measurement of both basic characteristics was combined in experiments of four types:

1) Oxygen chemisorption measurements on the freshly activated catalyst. The catalyst sample was dried, activated at 400°C either by sulphidation with a hydrogen–hydrogen sulphide mixture or by the sulphidation with subsequent reduction with hydrogen, flushed with helium, subjected to tempering and then chemisorption was carried out.

2) Catalytic activity and oxygen chemisorption measurements on the catalyst surface in working state. The sample was dried and activated as previously described. The activated catalyst was cooled to 300°C and subjected to the 4·5 h reaction. After that, helium was introduced again into the reactor. After 5 min-flushing, the temperature was adjusted during 10 min to 400°C. The standard procedure of flushing, tempering, and chemisorption measurement followed.

3) Oxygen chemisorption measurements on reactivated catalyst. After the standard procedure of chemisorption measurement, the sample of the catalyst was warmed up to 400°C under flowing helium within 5 min. Helium was then replaced by sulphidation mixture or by hydrogen and the catalyst was reactivated for the period chosen. The reactivation was followed by the standard helium flushing, tempering and by the second chemisorption measurement. In experiment with repeated reactivation, the same procedure was repeated after the second chemisorption measurement and chemisorption was measured for the third time.

4) Catalytic activity and oxygen chemisorption measurements on the catalyst surface in working state on the reactivated catalyst. After measuring the chemisorption capacity of the catalyst in the standard way, the sample was reactivated as ad *3*) and then the reaction was carried out and oxygen chemisorption measured as ad *2*).

In all the experiments, the following identical conditions were maintained: The weighted amount of the catalyst was 0·5 g. Flow rate of hydrogen and ethylene were always 50 ml/min, that of hydrogen sulphide 5 ml/min. Helium flow rate in drying, flushing and catalyst tempering was 50 ml/min, in chemisorption measurements 30 ml/min. All the volumes mentioned above are those at 20°C and a pressure of 100 kPa. The values of chemisorption capacities and ethylene conversions presented in tables were obtained as the average of two to four experimental values, which fulfilled the requirement of the reproducibility. The exception are the results in Table VI, where the values obtained always in one typical experiment are presented. In all the pretreatment procedures used, the course of chemisorption measurements was the same, constant height of the oxygen peak was achieved after 18 to 22 pulses. In Results we present also the values of oxygen chemisorption measured on the reduced catalyst[6] by dynamic method at −78°C. Based on the studies by Bodrero and coworkers[5] and Liu and collaborators[12] we assume that the values obtained by pulse dynamic method for the reduced catalysts at −78°C and for the sulphided catalyst at 20−25°C are comparable to the values obtained for the reduced catalysts by a static method at −78°C and are thus comparable to each other.

RESULTS

Chemisorption and Catalytic Activity on Freshly Activated Surface

Table I presents results of experiments made with the aim to verify the dependence of chemisorption capacities A and A_p on sulphidation time. In accordance with the results of our previous work[11], the activity in hydrogenation of ethylene and chemisorption capacity depends on the time of sulphidation at 400°C only up to 30 min. The same holds also for the chemisorption on the surface in working state. It is also evident that for the given reaction, A and A_p are approximately equal on the sulphided catalyst. Although differences in the values smaller than 10% are not significant, it is still worth mentioning that in no case A_p was smaller than A. The results of the measurement in which sulphidation was followed by additional reduction by hydrogen for period of 15 to 120 min are given in Table II. Comparison of the values of A from Tables I and II shows that chemisorption on the surface activated by the combined process is higher (at maximum by 40%) than chemisorption on only sulphided surface and it increases with sulphidation time up to 60 min. It is also evident from Table II that when the additional reduction is carried out for the same time, the

same values of chemisorption are obtained after 10, 30 and 60 min — sulphidation. On the other hand, any significant effect of the additional reduction has not been observed in the case of the activity. At the sufficient sulphidation time (starting from 30 min), the steady ethylene conversion does not increase on further reduction, at short sulphidation (10 min) it attains only the values obtained by the longer sulphidation without additional reduction. The ratio of chemisorption on the freshly activated surface to that on the surface in working state is different for the sulphided-reduced catalyst and the catalyst which was only sulphided. Here, A_p is lower than A, even though A_p on the sulphided-reduced catalyst is still higher than A on the

TABLE I

Dependence of chemisorption capacity of freshly activated surface, catalytic activity and chemisorption capacity of catalyst surface in working state on sulphidation time

Sulphidation min	A ml g^{-1}	a	A_p ml g^{-1}
10	0·86	0·31	0·90
30	0·96	0·35	1·05
60	1·00	0·36	1·05
120	0·99	0·35	1·08

TABLE II

Dependence of chemisorption capacity of freshly activated surface, catalytic activity and chemisorption capacity of catalyst surface in working state on time of the additional reduction with hydrogen

Sulphidation min	H₂ reduction min	A ml g^{-1}	a	A_p ml g^{-1}
60	15	1·17	—	—
60	30	1·28	—	—
60	60	1·36	0·36	1·22
60	120	1·40	0·34	1·27
30	60	1·38	0·36	1·18
10	15	1·15	—	—
10	30	1·30	—	—
10	60	1·35	0·35	1·19
10	120	1·38	0·35	1·17

sulphided catalyst. Table III documents how different results can be obtained on the same catalyst only by variations of the activation process. It should be stressed that only values obtained under conditions where chemisorption capacity is no longer affected by the time of any step of the activation process are presented in Table III. It is apparent that while the steady conversion had the same value irrespective of different activation procedures, the chemisorption capacity depends markedly both on the activation procedure and on the fact whether it was measured on the freshly activated catalyst or on the catalyst in working state.

Chemisorption and Catalytic Activity on Reactivated Surface

In practice, chemisorption measurements or catalytic activity tests are often performed after the previous passivation of the catalyst by air oxygen and its reactiva-

TABLE III

Dependence of chemisorption capacity of freshly activated surface, catalytic activity and chemisorption capacity of catalyst surface in working state on the procedure of activation

Procedure	A ml g^{-1}	a	A_p ml g^{-1}
Reduction H$_2$ 8h/500°C^a	0·80	0·34	0·38
Sulphidation H$_2$/H$_2$S 1h/400°C	1·00	0·35	1·05
Sulphidation H$_2$/H$_2$S 1h/400°C and additional reduction by H$_2$ 1h/400°C	1·35	0·36	1·22

^{a} Taken from ref.[6]; values of chemisorption capacities obtained by dynamic method at $-78°C$.

TABLE IV

Dependence of chemisorption capacity, catalytic activity and chemisorption capacity of catalyst surface in working state on the procedure of reactivation

Sulphidation min	A ml g^{-1}	Resulphidation min	Reactivation by H$_2$, min	A_{rl} ml g^{-1}	a_r	A_{pr} ml g^{-1}
60	0·95	--	--	—	0·36	0·98
60	0·98	60	--	0·91	0·38	0·99
60	0·98	—	60	1·34	0·36	1·22
10	0·83	—	60	1·28	0·32	1·15

tion. We wished therefore to get information on the behaviour of the surface reactivated after the preceding primary activation and oxygen chemisorption and also to find out whether the effect of hydrogen in the activation process is the same also after its interruption by oxygen chemisorption. The results in Table IV show that even without a special process of reactivation (data in the 1st line of Table IV), the catalyst reactivates in the reduction atmosphere of the hydrogenation reaction during several minutes so that the reaction course and the value of steady conversion do not differ from the values obtained for the freshly sulphided catalyst. The same holds also for the chemisorption on the surface in working state. The other results vary widely, depending on the reactivation procedure. After reactivation by sulphidation, chemisorption on reactivated surface does not attain the value obtained after the first sulphidation, while the activity and cl emisorption on the surface in working state do not differ from the values found on the freshly sulphided surface. On the reactivation with hydrogen, chemisorption on the reactivated surface is markedly higher compared to the freshly sulphided catalyst. Chemisorption on the reactivated surface in working state, A_{pr} is lower than A_{r1}, even though it is still higher than A. Only the activity of the catalyst is again unchanged. In the experiment with a short sulphidation, even after 1 h-reactivation, the activity remained at the lower value which corresponds to the activity on the freshly sulphided catalyst. From these experiments it is obvious that the most distinct effect occurs in the case of the reactivation by hydrogen. Except the experiment with the short sulphidation, the results are very similar to those obtained by direct sulphidation-reduction.

We have measured the dependence of chemisorption capacity on the time of reactivation by hydrogen at 60 min-sulphidation. The results are given in Table V. Comparison of the corresponding values of chemisorption capacities (A from Table II and A_{r1} from Table V) show that except the shortest times of reactivation, additional

TABLE V

Dependence of chemisorption capacity of the reactivated catalyst on time of reactivation by hydrogen

Sulphidation min	A ml g^{-1}	Reactivation by H₂, min	A_{r1} ml g^{-1}
60	0·95	15	1·01
60	1·00	30	1·27
60	0·96	60	1·34
60	0·95	120	1·35

reduction or sulphidation, the effect of hydrogen on reactivation is the same as in direct additional reduction. Analogical relationships were also observed for the chemisorption on the surface in working state (compare A_p from Table II and A_{pr} from Table V). In contradistinction to the chemisorption capacity, the catalytic activity after sufficiently long sulphidation is not affected either by the additional reduction or by the reactivation. After short sulphidation (10 min), the reactivation did not result in small increse of catalytic activity which occurs when the surface is subjected to additional reduction.

The results of the experiments in which the reactivation after chemisorption measurement was repeated twice are given in Table VI. It is obvious that the second resulphidation has the same effect as the first one. The reactivation by hydrogen shows the same effect on both freshly sulphided and resulphided surface. On the surface once reactivated by hydrogen for a sufficiently long time, the repeated reactivation did not lead to further increase in chemisorption capacity, while after short reactivation it did.

Based on these experiments and some results of our previous work[6], the most important facts can be summarized as follows: *1*) The catalyst in the sulphided form exhibits higher chemisorption capacity than that in the only reduced form. *2*) Exposure of the sulphided catalyst to hydrogen, both immediately after sulphidation and after its passivation by oxygen, increases further chemisorption capacity of the catalyst. *3*) Chemisorption capacity of the reduced and/or sulphided-reduced catalyst is lower after hydrogenation reaction than immediately after activation. Chemisorption capacity of the sulphided catalyst does not decrease after the reaction. *4*)Chemisorption capacity of the sulphided catalyst depends strongly on the activation procedure, its activity in the hydrogenation reaction does not.

TABLE VI

Dependence of chemisorption capacity of the reactivated catalyst on the procedure of first and second reactivation

Sulphidation min	A ml g^{-1}	Resulphida- tion min	Reactivation by H$_2$, min	A_{r1} ml g^{-1}	Resulphida- tion min	Reactivation by H$_2$, min	A_{r2} ml g^{-1}
60	0·95	60	—	0·92	60	—	0·89
60	0·98	60	—	0·91	—	60	1·34
60	0·95	—	15	1·06	—	60	1·27
60	1·01	—	60	1·33	—	60	1·33

DISCUSSION

Effect of Activation Procedure on Chemisorption Capacity of Catalyst

The higher chemisorption capacity of the sulphided catalyst (with or without additional reduction) compared to the only reduced catalyst is the result opposite to that reported by Fierro and coworkers[3]. This difference can again be explained by different conditions used in the activation process rather than by the different methods used in chemisorption measurements. In the case of the sulphided catalyst[3], activation temperature of 450°C gives possibly rise to changes in the dispersion of the supported phase. We have chosen intentionally different temperature of activation for the reduced[6] and sulphided catalyst (500 and 400°C respectively), with the aim to achieve by both ways the fully activated and pure surface, however, without dramatic structural changes of the active phase in the case of the sulphided catalyst. We proved earlier[7] that at 400°C the active component of the catalyst does not tend to change dispersion and that the catalyst surface at this temperature is also sufficiently purified. The only significant effect which could be expected for our catalyst as the result of the different activation procedures is the change of the chemical composition of catalyst surface.

Effect of Hydrogen on Sulphided Catalyst

The increase of chemisorption capacity of the sulphided catalyst if it is exposed to hydrogen at the end of the activation is not surprising. In the works mentioned in the introduction, the catalysts based on MoS$_2$ also showed higher chemisorption capacity after reduction with hydrogen under mild temperature conditions or after sulphidation-reduction than after the activation effected only by sulphidation. (Also in this work the effect of resulphidation of the already sulphided catalyst was rather negative). Although details of the processes proceeding on the surface of MoS$_2$ and on the surface of sulphided supported catalyst will be different, the basic effect of the arrangement of the activation procedure is possibly the same. The reasons of such an agreement will be yet discussed.

Chemisorption Capacity of Catalyst in Working State

The result, which is unexpected on the basis of the so far reported studies, is the same value of A and A_p on the sulphided catalyst and/or equal A and A_{pr} on the resulphided catalyst. If the decrease of chemisorption capacity after the reaction in all the other cases has a common reason (this being a process taking place during the reaction) then here it must be hidden by another process proceeding simultaneously. In any case, it becomes evident that the lower value of chemisorption capacity on the surface in working state is not general phenomenon for the sulphided catalysts,

and the A/A_p ratio depends on the procedure of activation. The presumption of Tauster and coworkers[4] that A_p is a more representative characteristics of the catalyst then A can anyhow be accepted. However, one has to take into account that by measuring A_p only, one of important advantages of the chemisorption method is eliminated, i.e. getting certain prognosis of the catalytic activity without measuring it directly.

Correlation of oxygen chemisorption with catalytic activity has not been found for the sulphided catalyst. It should be stressed that here the lack of correlation has another reason than in the most cases reported earlier where this lack was caused predominantly by the factors which affected catalytic activity, while the chemisorption was insensitive to these factors. The independent variable chosen by us, i.e. the activation procedure, affected chemisorption, but no relationship was observed between its changes and catalytic activity. On the basis of our recent and previous results and some literature data, we offer explanation of the presumable reasons responsible for the difference in the sensitivity of oxygen chemisorption and hydrogenation reaction to the activation procedure in the case of our catalyst.

Structure and Interrelations between Active Sites for Chemisorption of Oxygen, Hydrogenation and Hydrodesulphurization Reaction

The chemisorption of oxygen as well as hydrogenation (HYD) and hydrodesulphurization (HDS) reaction occur only on specific active sites. Concerning their structure and function, the following ideas have been generally accepted:

On molybdenum-based supported HDS catalysts, the active sites are coordinately unsaturated sites (CUS), formed by molybdenum atom in the oxidation state lower than 6^+. The active phase of sulphided catalyst is present on the supported surface as dispersed MoS_2-like structure, the form of which, in dependence on molybdenum content, passes from monolayer patches to multilayer crystallites. CUS exist on the edge planes or corners of these crystallites. It seems likely that they are of several types[4,13,14] and have different intrinsic activity for different types of processes. Oxygen is chemisorbed on all the sorts of these CUS, i.e. it is not capable of "distinguishing" the deviations in structure details as well as it does not differentiate the intrinsic activity for other processes. Therefore, by chemisorption of oxygen, one cannot detect the effect of factors which lead to qualitative changes in the vicinity of molybdenum atom, such as for instance the number of neighbouring atoms, the presence of promotor or the change of interaction between molybdenum atom and support[13,15]. These factors manifest themselves most in HDS reaction since its mechanism is most complicated. HYD reaction is somewhat less sensitive, and the oxygen chemisorption is essentialy nonselective. Therefore, on a given catalyst, promotor increases markedly HDS activity, less the activity in HYD, the oxygen chemisorption being practically the same[13]. Most likely for that reason, the better

correlations have been often found for oxygen chemisorption and HYD reaction then for the chemisorption and HDS reaction.

On Possible Participation of SH *Groups in Oxygen Chemisorption on Sulphided Catalysts*

Our results demonstrate the failure of the correlation between oxygen chemisorption and HYD reaction activity on the sulphided catalyst in dependence on the activation procedure. As the quantity and intrinsic activity of the sites for HYD reaction remain obviously unchanged, some procedures have therefore to lead to the increase in the number of chemisorption active sites which are absent on the catalyst after reduction (as follows from the results reported earlier[6]) and which are not active in HYD reaction. We believe that the sites of this kind can be connected to SH groups which — under our activation conditions — are formed by the reaction of hydrogen sulphide and hydrogen with the catalyst surface. Both these paths of formation of SH groups at 400°C were confirmed by us experimentally[11], on following the concentration of SH groups on catalyst surface in the isothermal sulphidation at different temperatures and the dependence of partial pressures of hydrogen, hydrogen sulphide and water on temperature in the temperature-programmed reductive sulphidation of the same catalyst. The development of active sites for oxygen chemisorption showed a similar course as the development of the SH group concentration. We thus concluded[11] that SH groups are formed at 400°C both by the reaction of hydrogen sulphide with surface oxides of the catalyst and by the reaction of hydrogen with the sulphides. The sites active in oxygen chemisorption are formed either by decomposition of the surface molybdenum (oxy)sulphides to give sulphur and the reduced molybdenum (this reaction is proposed also by Arnoldy and coworkers[16]) or by the reaction of hydrogen with the sulphides via the intermediate which are surface SH groups. Stuchlý and Beránek[17] found a good correlation between oxygen chemisorption and the activity of the sulphided catalyst in HYD reaction and also between this activity and the concentration of SH groups. However, similarly high activity was exhibited also by the catalyst not containing SH groups which was reduced only by hydrogen. This indicates that the development of the active sites for the reaction only parallels the development of SH groups and is not closely related to it. Notwithstanding, the catalysis of HDS reactions[17–20] has been proposed to be related to SH groups and a similar relation cannot be excluded also for oxygen chemisorption. If the sulphided catalyst surface is exposed to hydrogen without presence of hydrogen sulphide in gas phase, further SH groups are formed through hydrogen dissociation on CUS at the edge planes of crystallites of the active phase and its subsequent chemisorption on its basal planes[15,21–23] in the form of SH groups. The SH groups as functional sites for oxygen chemisorption on the sulphided Mo/Al₂O₃ catalyst were proposed already by Bachelier and collaborators[20]. The authors measured

chemisorption at 60°C, and proposed a mechanism involving dissociation of oxygen molecules to atoms reaching subsequently the CUS and SH group bonded to the same molybdenum atom. The isolated SH groups are considered as insensitive to oxygen. This mechanism is obviously connected with given specific conditions. Oxygen chemisorbs as well on CUS without participation of any SH groups on the catalyst reduced by hydrogen at low temperature. With our attempt to accomplish oxygen chemisorption at 60°C on our sulphided catalyst, the behaviour characteristic rather for the subsurface reaction than for the surface reaction was found[7]. However, we believe that on sulphided $(Co-)Mo/Al_2O_3$ catalysts, even at 20°C a certain part of SH groups on the catalyst surface acts pressumably as another type of oxygen chemisorption sites. While the catalytic activity in HYD reaction appears to be a function of only CUS concentration, in this case the chemisorption capacity is the function of both the CUS concentration (the sites on which oxygen dissociation and predominant part of its chemisorption takes place) and of the concentration of active SH groups. This could explain the sensitivity of oxygen chemisorption to those parameters of the activation process which affect the concentration of SH groups on catalyst surface, regardless whether MoS_2 or supported molybdenum catalyst is concerned.

The chemisorption capacity of our $Co-Mo/Al_2O_3$ catalyst increased in the sequence reduced < sulphided < sulphided-reduced catalyst due to the formation of active SH groups which first appear due to the reaction of the catalyst with hydrogen sulphide and their number then increases by the reaction of the sulphided surface with hydrogen in the absence of hydrogen sulphide in the gas phase. The final CUS concentration is the same in all the activation procedures (although they are formed by different mechanism and at different rates) and hence also the activity in hydrogenation of ethylene is identical. Only in the case of imperfect, too short sulphidation, hydrogen can complete the reduction of the molybdenum atoms capable of CUS formation. This results then in the enhancement of initially lower catalyst activity, however, only to the value corresponding to the activity of the perfectly sulphided catalyst. The same reasoning can be applied to the results obtained in experiments with the reactivated catalyst. The increase of SH concentration on surface of the sulphided catalyst in the reductive medium of hydrogenation reaction can most likely account for the fact that the chemisorption capacity of this catalyst does not decrease after the hydrogenation reaction.

The participation of the two types of functional sites in oxygen chemisorption can account for the fact that the correlation of oxygen chemisorption with catalytic activity in HYD reaction, examined in dependence on activation conditions, is good, if only one type of functional sites is developed during activation or the sites of both types are formed simultaneously, while in cases where both types of functional sites develop independently, the correlation fails. In our studies of the activation process we have observed in two cases a significant dependence of chemisorption capacity

on the time of activation process or on a certain step of the process. The capacity increase with reduction time[6] was caused by the increase in CUS concentration and oxygen chemisorption correlated well with the catalytic activity in HYD reaction. The increase of chemisorption capacity of the sulphided catalyst with time of the additional reduction (or of the reactivation by hydrogen) found in this work can be related to the increase of the concentration of active SH groups, but not of CUS. That is why we observed only the increase of chemisorption, which was, however, in no correlation with the activity in HYD reaction.

CONCLUSION

We assume that, alongwith CUS, also some SH groups are involved in oxygen chemisorption as functional sites on sulphided (Co–)Mo/Al$_2$O$_3$ catalysts. Therefore, only information on the total number of active sites of both types can be obtained from oxygen chemisorption on these catalysts, not information on the number of CUS only. Both types of functional sites can be formed (or destroyed) during the activation process by mutually independent reactions and their final number depends on activation conditions. Similarly, in the course of HYD reaction, an additional development or desactivation of both types of functional sites can be expected, too. Hence, on studying correlations of oxygen chemisorption with catalytic activity and drawing conclusions from their shape and quality, the above fact should be taken into consideration.

LIST OF SYMBOLS

A — chemisorption capacity (oxygen uptake per g of catalyst) of freshly activated catalyst
A_p — chemisorption capacity of catalyst surface in working state
A_{r1}, A_{r2} — chemisorption capacity of the reactivated surface after the first and second reactivation, respectively
A_{pr} — chemisorption capacity of the surface of the reactivated catalyst in working state
a — catalytic activity (steady conversion of ethylene to ethane)
a_r — catalytic activity of the reactivated catalyst

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Translated by J. Hetflejš.