RESPONSE IN THE CATALYTIC PROPERTIES TO PRESULPHIDATION FOR PROMOTED AND NONPROMOTED MOLYBDENUM HYDROREFINING CATALYSTS

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The sensitivity of nonpromoted and promoted molybdenum catalysts to presulphidation was examined on the adsorption of hydrocarbons and pyridine, hydrodesulphurization of thiophene and benzothiophene, and cracking and dehydrogenation of isopropylbenzene. Published data of other authors concerning the hydrodesulphurization of thiophene and benzothiophene and hydrogenation of cyclohexene were also evaluated. In all cases except the dehydrogenation of isopropylbenzene, the change in the adsorption properties and catalyst activity brought about by the presulphidation were lower for the nonpromoted catalysts than for the promoted ones, thus indicating that cobalt is directly involved in the active surface of $CoMo/Al_2O_3$ catalysts.

The nature of the promoting effect of cobalt or nickel in molybdenum hydrorefining catalysts is so far not understood deeply enough[1-3]. Considerable amount of data has been obtained by physical methods concerning the effect of the promotor on the structure and the inorganic chemistry of the catalyst, but these on their own fail to offer an explanation of the reaction acceleration by the promotor. The changes induced by the promotor in the chemical behaviour of catalyst in its interaction with the reactants have received less systematic interest.

The principal change effected by a promotor in the chemical behaviour of a catalyst, as has been many times reported, is an enhanced catalyst activity. Clearly, this increase in activity cannot be accounted for by the enlarged active surface solely; in fact, the catalyst is altered qualitatively, a number of its chemical properties of intensive nature, such as the intermediates distribution in hydrodesulphurization reactions[4,5], the catalyst reducibility, surface acidity, *etc.*[1-3], being also changed.

In this paper it will be demonstrated that the extent to which the adsorption and catalytic properties are varied by presulphidation is greater for a promoted catalyst than for a nonpromoted one. This is in relation to the fact reported recently[2,6,7], that the effect of promotors is more appreciable for the presulphided form of a catalyst than for its oxidic form, and bears out the concept of changes occuring not only in the quantitative aspects, but also in the quality of the catalyst surface when a promotor is introduced. The data treated comprise our as yet unpublished results (adsorption of benzene and heptane, hydrodesulphurization

of benzothiophene and thiophene) together with our data published previously (adsorption of pyridine, decomposition of isopropylbenzene), and also data of other authors (hydrodesulphurization of thiophene and benzothiophene, hydrogenation of cyclohexene).

EXPERIMENTAL

The catalysts were prepared by conventional impregnation of commercial supports; two commercial promoted catalysts were also examined. All of the catalysts, and also the supports before impregnation, were ground to a grain size of 0·16—0·31 mm. The characteristics of the catalysts are summarized in Table I. A portion of each catalyst was presulphided by one of the two following procedures: Procedure (A): N_2, 400°C, 1 h; $H_2S + H_2$ (1 : 8), 400°C, 4 h; cooling down to room temperature under N_2, 1 h; Procedure (B): $N_2 + H_2$ (10 : 1), 450°C, 30 min; H_2, 450°C, 2 h; cooling down to 300°C, 30 min; $H_2S + H_2$ (1 : 10), 300—450°C, 30 min; $H_2S + H_2$ (1 : 10), 450°C, 3 h; cooling down to room temperature under N_2, 30 min. In both cases the presulphided samples were stored in air.

Adsorption of benzene and heptane. The reversible adsorption of the hydrocarbons at 150°C was monitored by the conventional chromatographic method[8] as described previously[9]. The catalyst was heated at 400°C under helium for 2 h and then cooled down to the temperature of measurement. The hydrocarbons were spiked by using a microsyringe, and the retention curves were processed conventionally[8-10] to give the isotherms over the pressure region of 0—2 kPa. The adsorption was reversible and the catalyst properties were steady, *i.e.* independent of the spiking order.

TABLE I
Characteristics of the catalysts used

Chemical nature	Type (origin)	Content, % (m/m), of		
		CoO	NiO	MoO_3
Al_2O_3 (I)	CHEROX 33-00[a]	—	—	—
Al_2O_3 (II)	HO 417[b]	—	—	—
Mo/Al_2O_3 (I)	laboratory	—	—	12
Mo/Al_2O_3 (II)	laboratory	—	—	13·7
$CoMo/Al_2O_3$	CHEROX 36—01[a]	3·5	—	13
$CoMo/Al_2O_3$ (I)	laboratory	3	—	12
$NiMo/Al_2O_3$	KETJENFINE 153—1·5 E[c]	—	3	15
$NiMo/Al_2O_3$ (II)	laboratory	—	3·3	13·2

Manufacturer: [a] Chemical Works, Litvínov, Czechoslovakia; [b] Houdry Hüls, FRG; [c] Akzo Chemie, Ketjen Catalysts, The Netherlands.

Adsorption of pyridine. The adsorption was measured on a conventional McBain type balance by the procedure described in detail in ref.[11]. The sample was heated at 400°C in a vacuum of the order of 10^{-3} Pa for 6 h and then cooled down to the temperature of measurement, 300°C. The partial pressure of pyridine was gradually raised from 9·3 Pa up to 2·4 kPa and the mass increments were determined. The reversibility of adsorption was not examined in detail and seemed to be partial only.

Hydrodesulphurization of thiophene. A high-pressure flow-through tubular microreactor was used as described previously[12]. The catalyst was heated in a stream of hydrogen at 2·1 MPa. After attaining a temperature of 200°C, the feed of a 20% mol. solution of thiophene in decane was started, and the temperature was raised up to that of reaction, 320°C. The components fed were present in a molar ratio of thiophene: decane : hydrogen = 1 : 4 : 70. The condensate at the outlet was sampled for gas chromatographic analysis. The conversion on the presulphided as well as oxidic samples became steady in approximately 1 h of feed; the monitoring was continued for another 1 h.

Hydrodesulphurization of benzothiophene. The reaction was examined in the same reactor as the hydrodesulphurization of thiophene. The reaction temperature was 270°C, total pressure 2·1 MPa, the components fed were in the ratio of benzothiophene : decane : hydrogen = 1 : 5 : 47 (the whole was present in the gaseous state). The measurement procedure was similar as for thiophene, and has been described in detail elsewhere[13]. The conversion on the presulphided samples became steady in 30 min, the activity of the oxidic samples increased slowly to reach the steady state only in 2—3 h.

Cracking and dehydrogenation of isopropylbenzene. The reaction was followed in a pulse reactor at 400°C in an inert at atmospheric pressure[11]. For each sample, the conversion was monitored in dependence on the gas flow rate at a constant pulse magnitude. The catalyst activity and selectivity depended on the pulse order and were extrapolated to the zeroth pulse[11].

RESULTS

Adsorption of benzene and heptane. The isotherms were obtained for the oxidic as well as the presulphided forms of the $Mo/Al_2O_3(I)$ and $CoMo/Al_2O_3(I)$ catalysts

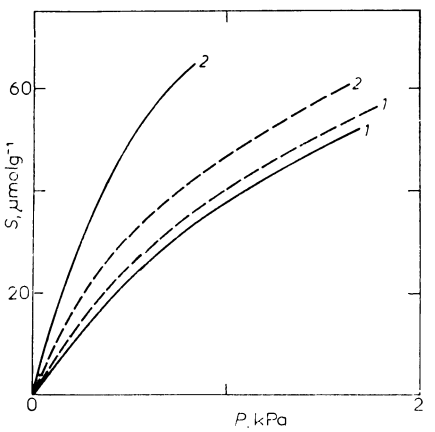

FIG. 1

Adsorption isotherms of benzene on $Mo/Al_2O_3(I)$ (– – – –) and $CoMo/Al_2O_3$ (————) catalysts at 150°C; *1* oxidic form, *2* presulphided form

over the hydrocarbon partial pressure region of 0–2 kPa. The results for benzene are shown in Fig. 1, the data for heptane were similar. The isotherms were compared by the procedure derived in detail previously[10]. The difference in the adsorption of the hydrocarbon on the sulphurized, (s), and the oxidic, (o), forms of catalyst was characterized by the difference between the chemical potentials, $\Delta\mu$, of the hydrocarbon adsorbed on the two forms in the same quantity. The more negative the $\Delta\mu$ value, the more the presulphided form adsorbs in comparison with the oxidic form. Similarly as for other catalyst types[9,10], the $\Delta\mu$ difference was independent of the sorbed amount. As a bonus, this approach requires no mathematical description of the adsorption isotherm. The results of this comparison are given in Table II. Two facts are of interest: first, the presulphided form adsorbed invariably more than the oxidic form ($\Delta\mu$ was negative), and second, the difference between the two forms was considerably higher for the promoted catalyst than for the nonpromoted one.

Adsorption of pyridine. The experimental adsorption isotherms were fitted by the Langmuir isotherm by applying the procedure[11]. The maximum adsorbed amounts obtained were little dependent on the sample form; the differences in the adsorption manifested themselves particularly in the adsorption constant K. The two forms are compared in Table III, giving the ratio of the adsorption constants on the presulphided (K (s)) and on the oxidic (K (o)) forms along with the corresponding difference in the free enthalpies of adsorption $\Delta(\Delta G^0_{ads})$. The adsorption on the support itself and on the nonpromoted catalyst was unaffected by the sulphidation. In the presence of promotor in the molybdenum catalyst, on the other hand, the sensitivity of adsorption to presulphidation increased significantly.

Hydrodesulphurization of thiophene. The conversion was examined on a nonpromoted laboratory sample and on promoted laboratory as well as commercial catalysts in the presulphided (s) and the oxidic (o) forms. The data were evaluated to give the first order rate constants k(s) and k(o) whose ratios, as given in Table IV,

TABLE II

Differences in the chemical potentials of hydrocarbons adsorbed on presulphided and on oxidic catalysts; sulphidation by procedure (B)

Catalyst	$\Delta\mu$, kJ mol^{-1}, of	
	benzene	heptane
Mo/Al_2O_3 (I)	−0·72	−2·58
$CoMo/Al_2O_3$ (I)	−2·42	−4·51

were treated to give the differences between the free enthalpies of activation on the two forms of catalyst (Table IV). The catalyst activity increased with presulphidation particularly for the promoted samples, although for the nonpromoted ones some increase could also be observed. Also, the $k(s)/k(o)$ ratios for another twelve promoted commercial and pilot-plant samples measured previously[14], laying in the region of 3–6·5 (4·1 in average), were invariably higher than that obtained on the non-promoted $MoAl_2O_3$ sample as given in Table IV.

TABLE III

Comparison of the adsorption of pyridine on presulphided and oxidic catalyst samples; sulphidation by procedure (*A*)

Catalyst	K (s)/K (o)	$\Delta(\Delta G^\circ_{ads})^a$ kJ mol^{-1}
Al_2O_3(II)	1·03	−0·14
Mo/Al_2O_3(II)	1·00	0·00
$NiMo/Al_2O_3$(II)	1·36	−1·47
$CoMo/Al_2O_3$	1·25	−1·07
$NiMo/Al_2O_3$	2·25	−3·87

[a] $\Delta(\Delta G^\circ_{ads}) = -2{\cdot}3RT \log [K(s)/K(o)]$.

TABLE IV

Comparison of the rate constants of hydrodesulphurization on presulphided and oxididic catalyst samples for thiophene and benzothiophene; sulphidation by procedure (*B*)

Catalyst	k (s)/k(o)	$\Delta(\Delta G^{\neq})^a$ kJ mol^{-1}
	Thiophene	
Mo/Al_2O_3(I)	2·1	−3·67
$CoMo/Al_2O_3$(I)	6·3	−9·11
$CoMo/Al_2O_3$	4·9	−7·87
	Benzothiophene	
Mo/Al_2O_3(I)	1·2	−0·82
$CoMo/Al_2O_3$	3·5	−5·66

[a] $\Delta(\Delta G^{\neq}) = -2{\cdot}3RT \log [k(s)/k(o)]$.

Hydrodesulphurization of benzothiophene. The two forms of a nonpromoted laboratory sample and a promoted industrial catalyst were tested. For the presulphided promoted sample the complete integral curve of degree of conversion *vs* reciprocal space velocity was measured. The data could be well fitted by a rate equation of the 1·5th order with respect to benzothiophene; this equation was employed to calculate the k(s) and k(o) rate constants for the remaining samples based on the corresponding degrees of conversion; their ratios along with the differences in the $\Delta G^{\ddagger}$ values are also given in Table IV. Again, the difference between the two forms was considerably higher for the promoted than for the nonpromoted catalysts.

Cracking and dehydrogenation of isopropylbenzene. The reaction was investigated on one nonpromoted and three promoted samples. For each catalyst the degrees of conversion were measured at three different carrier gas flow rates, and the 1st order rate constants of cracking, k_C(s) and k_C(o), and of dehydrogenation, k_D(s) and k_D(o), were calculated. The values are given in Table V along with the selectivities defined as $Y = k_C/k_D$. For the cracking reaction the change in the catalyst activity brought about by the presulphidation treatment increases if promotor has been added, similarly as in the above adsorptions and reactions, but in the case of the dehydrogenation the reverse is true. As a result, the changes in selectivity observed on the two forms of catalyst are mutually opposite: while on the promoted samples the selectivity increases on sulphidation, on the nonpromoted samples the selectivity decreases.

DISCUSSION

The fact that the promoting effect is higher on presulphided catalysts than on oxidic ones has been described recently[2,6,7]. This can be formally written as

TABLE V

Comparison of the activity and selectivity of isopropylbenzene decomposition on presulphided and oxidic catalyst samples; sulphidation by procedure (*A*)

Catalyst	k_C (s)/k_C (o)	$\Delta(\Delta G_C^{\ddagger})^a$ kJ mol^{-1}	k_D (s)/k_D (o)	$\Delta(\Delta G_D^{\ddagger})^a$ kJ mol^{-1}	Y (s)^b	Y (o)^c
Mo/Al_2O_3(II)	1·06	− 0·38	7·51	−13·0	2·4	16·8
$NiMo/Al_2O_3$(II)	1·30	− 1·70	0·93	0·47	20·7	14·8
$NiMo/Al_2O_3$	3·24	− 7·59	0·34	6·97	50·2	5·3
$CoMo/Al_2O_3$	15·3	−17·6	3·17	− 7·46	7·5	1·6

[a] $\Delta(\Delta G^{\ddagger}) = -2{\cdot}3RT \log [k\,(s)/k(o)]$; the subscripts C and D refer to cracking and dehydrogenation, respectively; [b] $Y\,(s) = k_C\,(s)/k_D\,(s)$; [c] $Y\,(o) = k_C\,(o)/k_D\,(o)$.

$$A(\mathrm{p,\,s})/A(\mathrm{n,\,s}) > A(\mathrm{p,\,o})/A(\mathrm{n,\,o})\,, \qquad (1)$$

where A is the catalyst property under consideration and the symbols p, n, s and o refer to the promoted, nonpromoted, sulphided, and oxidic forms, respectively. Alternatively, this relation can be put down in the form

$$A(\mathrm{p,\,s})/A(\mathrm{p,\,o}) > A(\mathrm{n,\,s})/A(\mathrm{n,\,o})\,, \qquad (2)$$

and hence, the statements "the activity response of the presulphided form of catalyst to the addition of promotor is higher than that of the oxidic form" and "the activity response of a promoted catalyst to presulphidation is higher than that of the nonpromoted catalyst" are equivalent. In the present work the catalysts were compared from the point of view of relation (*2*), hence, the two forms were compared of a promoted or nonpromoted catalyst; the alternative approach, *viz.* a comparison according to Eq. (*1*), could not be applied because for some promoted catalyst – nonpromoted catalyst pairs there were differences in the sample preparation. This applies, for instance, to the pair $Mo/Al_2O_3(I)-CoMo/Al_2O_3$ in the hydrodesulphurization of benzothiophene.

Eqs (*1*) and (*2*), in which the ratios of the property values are compared, are adequate if the property A has the character of the adsorption or rate constant. If, however, the property A bears the meaning of the adsorption or activation free enthalpy, then owing to its logaithmic nature it is the differences rather than rations that have to be compared; hence, Eq. (*2*) is replaced by the relation

$$|A(\mathrm{p,\,s}) - A(\mathrm{p,\,o})| > |A(\mathrm{n,\,s}) - A(\mathrm{n,\,o})|\,. \qquad (3)$$

The two catalyst forms in question have been referred to as the presulphided and the oxidic forms. This is not quite correct because the initially oxidic sample also becomes sulphided during the reaction due to the formation of hydrogen sulphide. However, in the reaction conditions applied (low temperature, low hydrogen sulphide concentration) the degree of sulphidation is substantially lower than on the samples subjected to the presulphidation treatment with the H_2S—H_2 mixture (higher temperature, higher hydrogen sulphide concentration); in fact, the term little sulphided form would be appropriate.

All the results are presented in summary in Fig. 2. It can be seen that with the exception of the dehydrogenation of isopropylbenzene where the nonpromoted catalyst is most sensitive to presulphidation, relations (*3*) or (*2*) are generally valid, *i.e.* a nonpromoted catalyst is less sensitive to presulphidation than the corresponding promoted sample. Obviously the active functions of a catalyst that participate in the phenomena studied are not entirely independent. This is evident for some

of the processes, the relation of the hydrodesulphurization of thiophene and benzothiophene for instance, and less straightforward for others, such as the relation between the adsorption of heptane and the hydrodesulphurization of benzothiophene, or adsorption of heptane and adsorption of pyridine. The detailed relation between the phenomena can be, of course, rather complex, but the similarity in the response of the diverse processes to presulphidation indicates that the concept of highly specialized catalytic sites (sites for HDS, for hydrogenation, acid centres, *etc.*) is questionable and that the various functions of a catalyst cannot be completely separated from one another. A centre that takes part in all the adsorptions and reactions mentioned may be, for instance, an anionic vacancy on the catalyst surface.

The same effect can be found also in the data of other authors. The discussion in the original papers, if any, was always based on relation (*1*) *i.e.* the effect of promotor was compared in the presulphided and the oxidic forms. To enable them to be related to our data in Fig. 2, the original data were converted according to relations (*2*) and (*3*); the result of this treamtent is shown in Fig. 2.

Hagenbach and coworkers[7] desulphurized thiophene and hydrogenated cyclohexene on the two forms of a series of catalysts with various contents of promotor. Fig. 2 includes the data for the nonpromoted catalyst and for the catalyst with the Co/(Co + Mo) atomic ratio of 0·25, which is a typical composition of industrial catalysts. While for the nonpromoted catalyst the response to presulphidation was practically negligible, the activity of the promoted catalyst was substantially increased by the presulphidation.

De Beer and coworkers[15] subjected thiophene to desulphurization at atmospheric pressure on samples activated by various procedures. Fig. 2 includes the recalculat-

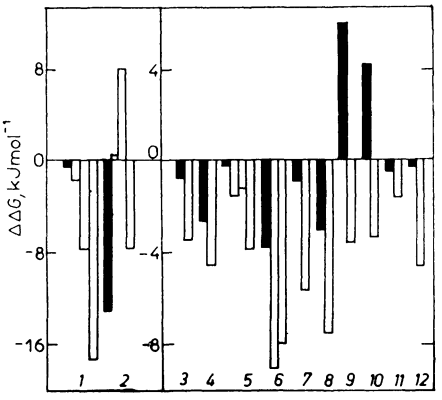

FIG. 2

Comparison of the differences between the free energies of adsorption or activation on presulphided and oxidic catalysts ($\Delta(\Delta G)$) for promoted (□) and nonpromoted (■) samples. *1*—*7* our data, *8*—*12* processing of published data: *1* cracking of isopropylbenzene, *2* dehydrogenation of isopropylbenzene, *3* adsorption of benzene, *4* adsorption of heptane, *5* adsorption of pyridine, *6* hydrodesulphurization of thiophene, *7*, *8* hydrodesulphurization of benzothiophene (ref.[6]), *9*—*11* hydrodesulphurization of thiophene (ref.[6,15,7], resp.), *12* hydrogenation of cyclohexene (ref.[7])

ed data for those samples that were air purged after the presulphidation, in agreement with our procedure. The activity of the nonpromoted catalyst was even lowered, while that of the promoted sample increased considerably.

A decrease in the activity for the reaction of thiophene after presulphidation of a nonpromoted catalyst was observed also by Bouassiada and coworkers[6]. In the reaction of benzothiophene, however, they observed an increase in activity for both the nonpromoted, and the promoted catalysts, the increase being substantially higher for the latter. Fig. 2 again shows the data for samples with the Co/(Co + + Mo) ratio of 0·25.

The data by Laine and coworkers[16] for the hydrodesulphurization of thiophene indicate that promotor has practically the same effect in the oxidic and in the presulphided forms of catalyst (comparison according to (*1*)). The data do not allow us to evaluate the ratios or differences according to Eqs (*2*) and (*3*), respectively, because the measurements on the two forms were accomplished at different temperatures.

The systematically different response of nonpromoted and promoted catalysts to presulphidation (or to increased sulphidation) gives evidence that cobalt plays a complex role not only in the formation of the oxidic precursor, but also in its transformation into the sulphidic state, and that it is directly involved in the active surface. This is consistent with the concept of different catalytic properties of surface sites including molybdenum in combination with cobalt as compared with molybdenum alone, as discussed by one of us elsewhere[17]. The results obtained fail, however to offer a detailed insight into the surface structure; this is to say that it is impossible to decide whether a phase contact is involved or whether a new phase, referred to[18,19] as Co—Mo—S, is formed.

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