MOLYBDENUM AREA AND HYDROGENATION AND HYDROGENOLYTIC ACTIVITIES OF HYDROREFINING CATALYSTS

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A series of nickel or cobalt promoted molybdenum catalysts and one nickel–tungsten catalyst have been studied by oxygen chemisorption on reduced oxidic samples, by activities of oxidic and sulphided samples for 1-hexene hydrogenation and by activities of sulphided samples for benzothiophen and pyridine hydrogenolyses. A good correlation was obtained between oxygen chemisorption and hydrogenation activity on oxidic, partially reduced, forms of the catalysts, and a limited correlation for activities of sulphided forms. Parallel activities for hydrogenation and hydrogenolyses were observed.

Low temperature chemisorption of oxygen on reduced molybdenum containing catalysts has been used for determination of "specific molybdenum area"[1–12]. The samples were either reduced molybdenum trioxide–alumina or molybdenum trioxide-cobalt oxide-alumina preparations and Tauster and coworkers[9–11] were able to extend the measurements to reduced and sulphided forms of an industrial Co-Mo-Al$_2$O$_3$ hydrorefining catalyst. The obtained chemisorption values have been successfully correlated with rate data for hydrogenation of alkenes[3,4], hydrogenolysis of sulphur compounds[9–12] and dehydrogenation of cyclohexene[6]. In most studies, the series of catalysts were closely related by origin; however, it has been shown recently[12] that the correlation between chemisorption of oxygen and catalytic activity holds also for Co-Mo–-Al$_2$O$_3$ catalysts prepared by various methods and in different compositions.

In the present paper, we have further examined this approach, which gives insight into the structure-activity relationships, using a series of less kindred hydrorefining catalysts. For the first time, catalysts containing nickel as promoter were studied and a Ni-W-Al$_2$O$_3$ catalyst was included for comparison. Oxygen chemisorption was measured at −78 °C in a pulse-flow apparatus[3] and a pulse-flow arrangement was used also for hydrogenation of 1-hexene at 350°C which served as the principal test reaction. The kinetic data on pressure hydrogenolysis of benzothiophen at 270°C and pyridine at 300°C were also compared with chemisorption values and 1-hexene rate data.

EXPERIMENTAL

Catalysts. Ni-Al$_2$O$_3$ (sample 1), Mo-Al$_2$O$_3$ (sample 2) and Ni-Mo-Al$_2$O$_3$ (sample 3) were prepared by impregnation of the Al$_2$O$_3$ carrier (HO 417, Houdry Hülls, surface area 222 m^2 g^{-1}) by solutions of nickel nitrate and ammonium heptamolybdate, respectively. Other catalysts were an experimental Ni-Mo-Al$_2$O$_3$-SiO$_2$ from the industry (Chemical Works, Litvínov, sample 5) and three industrial catalysts Ni-Mo-Al$_2$O$_3$ (Ketjenfine 153—1·5 E, sample 4), Co-Mo-Al$_2$O$_3$ (Cherox 36—01, Chemopetrol, Litvínov, sample 6) and Ni-W-Al$_2$O$_3$ (Cherox 34—02, Chemopetrol, Litvínov, sample 7). Their compositions and properties are summarized in Table I. The sulphided forms were prepared by treating the fractions 0·08—0·16 mm, obtained by crushing the pellets or extrudates and by sieving out, in a stream of gases using the following regime: 1 h in N$_2$ at 400°C, 4 h in H$_2$S-H$_2$ (1 : 8) at 400°C, cooling down to room temperature in nitrogen during 1 h.

Oxygen chemisorption (see[3]). Oxidic sample (0·5 g, particle size under 0·08 mm), mixed with approximately the same amount of glass balls, was placed into a glass U-tube, and the empty space was filled with glass balls. The apparatus was flushed with hydrogen (40 cm^3 min^{-1}) for 0·5 g at room temperature, then the U-tube was heated to 400°C during 1 h and maintained at this temperature for another 4 h. The hydrogen stream was changed for helium (30 cm^3 min^{-1}), after 0·5 h the U-tube was cooled to room temperature and placed into a solid CO$_2$-ethanol bath. After 45 min the flow of helium was equilibrated in both branches of the thermal conductivity cell and pulses of oxygen (0·22 cm^3) were periodically introduced into the stream of helium, until the oxygen peaks reached a constant height. Adsorbed volumes were corrected to STP conditions.

1-Hexene hydrogenation. Hydrogen serving as the reactant and carrier gas was purified in a deoxo unit and in a bed of molecular sieve. 1-Hexene (Carlo Erba chromatographic standard) was used without any treatment. The united reactor and gas chromatographic column consisted of a stainless steel tube (4·8 mm internal diameter) provided with a gas inlet and a septum. Its exit was connected to a thermal conductivity cell. The reactor zone was heated to 350 ± 3°C, the chromatographic zone to 200°C. The separation of the products was achieved on Al$_2$O$_3$ type F-1 (0·17—0·25 mm, length 1 500 mm). The reactor zone was charged with 0·05 to 0·15 g of oxidic or sulphided catalysts (0·08—0·16 mm) and before measurements, the catalysts were heated in hydrogen to 400°C for 4 h. Then the reaction temperature and hydrogen flow (35—50 cm^3 . min^{-1}) were adjusted and ten 0·5 µl pulses of 1-hexene were injected into the reactor. An example of product composition is shown in Fig. 1. The conversion was calculated from the area of hexane peak on the basis of calibration curves.

Benzothiophen hydrogenolysis. The procedure was described in detail in the previous paper[13].

Pyridine hydrogenolysis. The basic procedure by Černý[14] was used (100 cm^3 rocking autoclave, 0·5 g of the catalyst in sulphided form, 20 cm^3 of pyridine, 300 ± 5 °C, initial (cool) pressure 5·5 MPa). The product samples were analyzed in 1, 3 and 5 h by gas chromatography.

RESULTS AND DISCUSSION

The main product of 1-hexene hydrogenation was hexane and lighter hydrocarbons formed by cracking were observed only in small concentrations (Fig. 1). With catalysts 2 and 3, they amounted up to 5% of the main product, with other catalysts maximally to 2%. The kinetic data were obtained as dependences of conversion

Table I

Catalyst composition, surface area, oxygen chemisorption and rate constants of 1-hexene hydrogenation, benzothiophen and pyridine hydrogenolysis

Property	1 Ni–Al$_2$O$_3$	2 Mo–Al$_2$O$_3$	3 Ni–Mo–Al$_2$O$_3$	4 Ni–Mo–Al$_2$O$_3$	5 Ni–Mo–Al$_2$O$_3$–SiO$_2$	6 Co–Mo–Al$_2$O$_3$	7 Ni–W–Al$_2$O$_3$
Composition, wt.%							
NiO (CoO)	4·9	—	3·3	4·0	4·6	(3·5)	3·5
MoO$_3$(WO$_3$)	—	13·7	13·2	15·0	17·2	13·0	(27·0)
Al$_2$O$_3$	95·1	84·3	81·4	78·0	64·8	83·3	69·5
SiO$_2$	—	—	—	1·1	13·4	—	—
Surface area, m^2 h^{-1}	158	212	190	177	163	190	154
O$_2$, cm^3 (STP) g^{-1}	0·0	0·51	0·33	2·43	0·72	0·16	0·82
$k_{h,ox}$, cm^3 g^{-1} min^{-1}	—	83	43	328	84	0	35
$k_{h,sulph}$, cm^3 g^{-1} min^{-1}	—	79	119	279·	157	53	136
k_{BT}, mol g^{-1} MPa$^{0.5}$ h^{-1}	—	8·8	11·6	123·3	64·5	19·4	13·3
k_{PE}, g (h kg)$^{-1}$	—	1·82	0·93	2·23	1·56	0·57	1·32

to hexane on flow rate of hydrogen. They were fitted to the rate equation of the first order in respect to 1-hexene in integral form, assuming that the (unmeasured) space velocity of 1-hexene was proportional to the space velocity of the carrier gas. The result of the correlation is seen on Fig. 2 and the rate constants k_h on oxidic and sulphided catalysts, calculated as slopes of the lines, are given in Table I.
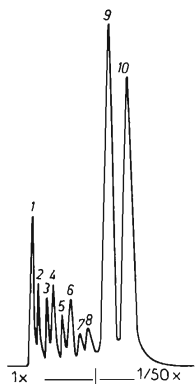

FIG. 1

Gas-chromatographic record of 1-hexene hydrogenation. Catalyst sample 4, reciprocal space velocity $2.6 \cdot 10^{-3}$ g min cm^{-3}. *1* Methane, *2* ethane + ethene, *3* propane, *4* propene, *5* butane, *6* butenes, *7* pentane, *8* pentene, *9* hexane, *10* hexene. For peaks *9* and *10* the sensitivity was diminished fifty times
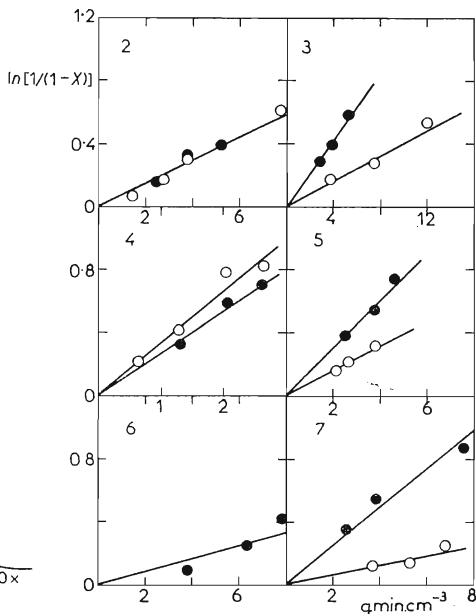
FIG. 2

First order plots of the conversions to hexane in 1-hexene hydrogenations. ○ Reduced oxidic catalysts, ● sulphided catalysts. The numbers correspond to sample numbers in Table I

The inspection of the k_h values shows that the effect of sulphidation varies within the series of the catalysts and the general trend is the diminishing of the differences in activities due to sulphidation. The most active sample 4 has lost some of its original high activity upon sulphidation whereas catalyst 6, almost non-active in oxidic form, has gained some activity. The correlations of hydrogenation activities with oxygen chemisorption, presented in Fig. 3a,b demonstrate this trend by smaller slope of the line for sulphided catalysts.

The correlation in Fig. 3a for the oxidic catalysts is fairly good with the exception of sample 7 based on tungsten, but the points in Fig. 3b for the sulphided catalysts
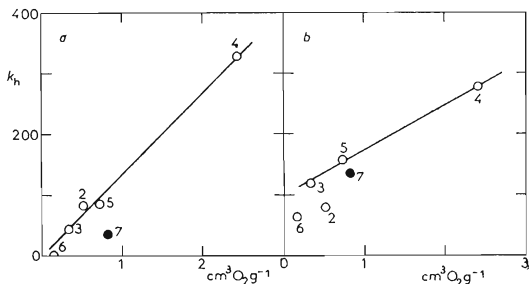

Fig. 3

Correlations of rate constant k_h on a) reduced oxidic and b) sulphided samples of catalysts (for identification of the numbers see Table I) with oxygen chemisorption on reduced oxidic catalysts
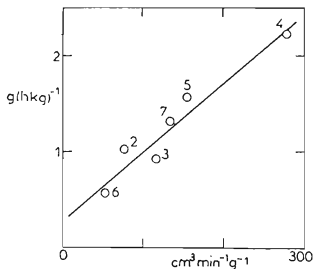

Fig. 4

Correlation of the rate constant k_{PE} for pentane + pentene formation from pyridine ($g\,h^{-1}\,kg^{-1}$) with the rate constant $k_{h,sulph}$ ($cm^3\,min^{-1}\,g^{-1}$) of 1-hexene hydrogenation on different catalyst samples (for identification of their numbers see Table I)

are rather scattered. However, the three nickel–promoted molybdenum catalysts fall on a line. The unpromoted and cobalt–promoted molybdenum catalysts and Ni–W–Al$_2$O$_3$ deviate.

Similar behaviour was observed when the same series of catalysts was tested by benzothiophen and pyridine hydrogenolyses. The set of data on benzothiophen reaction, given in part in previous paper[13], has been enlarged and treated by an integral kinetic rate equation of the order 1·5 to benzothiophen and zero order to hydrogen (for the equation see[12]). The calculated rate constants (270°C, 2·0 MPa) are given in Table I.

Pyridine hydrogenolysis at 300°C and 5·5 mPa yielded products described by Černý[14]. The conversions to C$_5$ hydrocarbons (pentane + pentenes) increased linearly with time during the 3 h interval and the slopes of this dependences were taken as the zero-order rate constants; their values are included into Table I.

Both k_{BT} and k_{PE} values show irregular trends in relation to oxygen chemisorption but similar behaviour as $k_{h,sulph}$. Especially the linear relationship between $k_{h,sulph}$ and k_{PE} is good (Fig. 4).

The present examination of the relation between oxygen chemisorption on reduced oxidic molybdenum catalysts and their catalytic activities for reactions involving hydrogen has shown that a) the linear correlation holds also for nickel–promoted molybdenum catalysts (until now, only cobalt promoted catalysts have been tested). b) the correlation is better when the samples are used for hydrogenation of 1-hexene in oxidic than in sulphided forms, c) as was expected, the nickel–tungsten catalyst behaved differently that the molybdenum based ones, d) there are parallelities in activities of sulphided catalysts in alkene hydrogenation, benzothiophen hydrogenolysis and pyridine hydrogenolysis.

The results of this work have shown that the influence of sulphidation on the activities of the hydrorefining catalyst can vary widely according to their original structure. This is connected very probably with formation of different active sites upon sulphidation of simple Mo sites and Mo sites promoted by Ni or Co; this problem of effective promotion will be dealt with in other paper[15].

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