

THE EFFECT OF SULPHIDATION ON THE NATURE OF ACTIVE SITES ON NICKEL-MOLYBDENUM-ALUMINA HYDROREFINING CATALYSTS

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A strong influence of sulphidation on the hydrogenation and hydrogenolytic activity of Mo-Al₂O₃ and Ni-Mo-Al₂O₃ hydrotreating catalysts has been found. Two kinds of active sites are distinguished, the first consisting of surface molybdenum atoms and serving mostly for hydrogenation, the second type formed by interaction of Mo with Ni atoms and being active in sulphided form for direct hydrogenolysis of the C-S bonds.

Recently, we have compared hydrogenation, dehydrogenation, hydrogenolytic and acido-basic properties of a series of hydrorefining catalysts¹⁻³, both in reduced oxidic and sulphided forms. Several correlations have been found between various characteristics of the catalysts, like cracking activity *vs* strength of pyridine adsorption¹, hydrogenation activity *vs* oxygen chemisorption on reduced samples² and hydrogenation activity *vs* rate of production of hydrocarbons from pyridine on sulphided samples¹. However, some peculiarities in trends appeared which we wish to interpret here as the results of transformation of the active sites on sulphided catalysts during their pretreatment.

EXPERIMENTAL

A consistent series of four unpromoted and nickel-promoted molybdenum catalysts will be discussed, omitting from the original series the cobalt-molybdenum and nickel-tungsten catalysts (*cf.*²; however, the original numbering of the catalysts is preserved here). Mo-Al₂O₃ (13.7% MoO₃, sample 2) and Ni-Mo-Al₂O₃ (3.3% NiO, 13.2% MoO₃, sample 3) were prepared by impregnation of the carrier. Another Ni-Mo-Al₂O₃ (3.0% NiO, 15.0% MoO₃, sample 4) was a commercial sample (Ketjenfine 153). Ni-Mo-Al₂O₃-SiO₂ (4.6% NiO, 17.2% MoO₃, 13.4% SiO₂, sample 5) was an industrial development preparation. All samples have been activated in the following way: 1 h in N₂ at 400°C, 4 h in H₂S-H₂ (1 : 8) at 400°C and 1 h in N₂ from 400°C to room temperature.

The activities of the sulphided catalysts have been measured by 1-hexene hydrogenation at 350°C in a pulse-flow apparatus after heating the catalysts in hydrogen for 4 h at 400°C (the activity is expressed as rate constant k_h in Table I), by dehydrogenation of isopropylbenzene to α -methylstyrene at 400°C in a pulse-flow apparatus after heating the catalysts in He for 2 h at 400°C (rate constant k_d) and by benzothiophen hydrodesulphurization at 280°C and 2.0 MPa in a flow apparatus, starting with sulphided catalysts which were reduced during the heating to the reaction temperature in hydrogen under pressure. The data on benzothiophen reaction are summarized in Table I as the rate constants of overall transformation (k_{BT}) and as the selectivity

ratios of the conversion to dihydrobenzothiophen (X_{DHBT}) to the overall conversion of benzothiophen (X_{BT}) to both products, *i.e.* to dihydrobenzothiophen and to ethylbenzene + hydrogen sulphide. The experimental details and the treatment of data are described in the previous papers^{1,2}.

RESULTS AND DISCUSSION

The results summarized in Table I show different trends in the values of the parameters. When going from sample 2 to 5, k_{h} and k_{BT} are increasing, whilst k_{d} and the ratio $X_{\text{DHBT}}/X_{\text{BT}}$ are decreasing. Two factors may be causing the observed differences in activities, either the nature of active sites or their concentrations. We wish to show here that these effects are interconnected and that, however, the nature of active sites has a predominating influence. The intrinsic cause for it seems to be the degree of effective promotion, that is the depth of the interaction between Mo and Ni which depends on the method of catalyst preparation.

The previous work^{1,2} where oxidic and sulphided catalysts were compared, has shown that the unpromoted Mo catalyst exhibits low activity both for hydrogenation and hydrogenolysis which is only little changed by sulphidation. This low sensitivity to the transformation of original sites, denoted here as (Mo-O), to (Mo-S) sites distinguishes them from the sites in nickel promoted catalysts (Ni-Mo-O) which increase their hydrogenolytic activity upon sulphidation to (Ni-Mo-S). However, the hydrogenation activity for alkenes of these new sites is small if any (residual hydrogenation activity could be ascribed to unpromoted Mo sites).

It is well known⁴ that the treatment of sulphide catalysts with H_2 at higher temperatures removes large amount of "mobile" sulphur from the surface. In our case, the catalysts were pretreated in this way and the evolution of H_2S was confirmed.

TABLE I

Summary of kinetic data on 1-hexene hydrogenation (k_{h} , $\text{cm}^3 \text{g}^{-1} \text{min}^{-1}$), isopropylbenzene dehydrogenation (k_{d} , $\text{cm}^3 \text{g}^{-1} \text{min}^{-1}$), benzothiophen overall reactivity (k_{BT} , $\text{mol g}^{-1} \text{MPa}^{0.5} \cdot \text{h}^{-1}$) and selectivity ratio ($X_{\text{DHBT}}/X_{\text{BT}}$ at $X_{\text{BT}} = 0.2$)

Sample ^a	2	3	4	5
k_{h}	79	119	157	279
k_{d}	308	74	35	21
k_{BT}	8.8	11.6	64.5	123.3
$X_{\text{DHBT}}/X_{\text{BT}}$	0.69	0.43	0.05	0.04

^a The numbering of the samples is consistent with previous papers¹⁻³.

In consequence, a reduced state of surface was formed, characterized by high hydrogenation activity with strongly promoted samples. On the opposite, k_d values were obtained after a treatment in He which is not able to remove important amounts of the surface sulphur; moreover, the k_d values were calculated from conversions extrapolated to the fresh surface, excluding thus the possible effect of the reduction by the reactant. Under this conditions, the dehydrogenation data refer to a reaction which had to proceed on different sites than the hydrogenation. The concentration of this sites decreased with the degree of effective promotion, *i.e.* with the increase in the concentration of (Ni-Mo-S). It can be concluded that the dehydrogenation sites are the (Mo-S) sites.

The data on benzothiophen can be interpreted in similar way. The ratio $X_{\text{DIBT}}/X_{\text{BT}}$ expresses the importance of the hydrogenation of benzothiophen to dihydrobenzothiophen in the overall reaction scheme

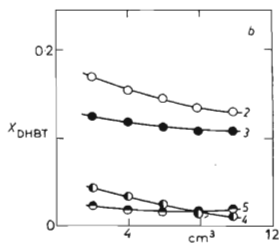
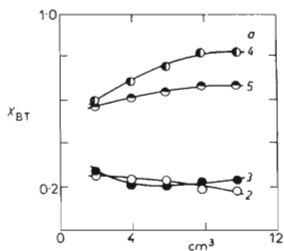
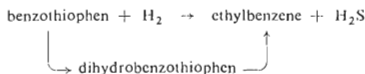


FIG. 1

Dependence of the overall conversion of benzothiophen a (X_{BT}) and of the conversion to dihydrobenzothiophen b (X_{DHBT}) on the volume of the feed passed through the reactor during the unsteady-state period (catalyst weight 0.1 g). Numbering of the curves corresponds to the numbering of the catalysts

The state of the surface, to which the data in Table I refer, corresponds to an equilibrium with sulphur contained in the feed and therefore, resembles more the state of the sulphided surface after treatment in He than the fully reduced surface obtained by H₂ treatment. Thus, the relative importance of the hydrogenation step decreases with effective promotion, whereas the overall activity (expressed as k_{BT}) increases.

Additional evidence for this interpretation is presented in Fig. 1, showing the approach to the steady-state during benzothiophen reaction with hydrogen on originally sulphided and reduced catalysts. The overall activity, k_{BT} , increases with highly active samples 4 and 5. With low-activity samples 2 and 3, an opposite behaviour is observed; in these cases, the important path in benzothiophen transformation is the hydrogenation to dihydrobenzothiophen which is not enhanced by the retention of the sulphur by the catalysts. On the other hand, the conversion to the hydrogenated intermediate is decreasing during this period.

The results reported here indicate that, in accord with the literature (*e.g.*⁵ and references given there), the hydrorefining catalysts possess two different kinds of active centres; one active centre for hydrogenation and the other one for direct hydrogenolysis of thiophenic ring. The number of the first kind is decreased by the interaction with a promoter and thus, it can be identified as the pure molybdenum site (Mo-O). Its activity is only little changed by sulphidation (Mo-S). In unreduced or mildly reduced form of the catalyst it can serve as dehydrogenating site. The nickel-molybdenum ensemble (Ni-Mo-O) is sensitive to sulphidation (Ni-Mo-S) which increases its activity for hydrogenolysis. We can speculate that cause of this sensitivity to sulphidation is easier reduction of the sulphided form. The strong influence of gas phase composition and especially of the content of sulphur compounds on the surface chemical structure has been demonstrated by Topsoe and coworkers⁶ recently.

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