

SYNERGISM IN HYDRODEAROMATIZATION OVER Ni-Mo/Al₂O₃ CATALYST

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Synergism in hydrodearomatization activity of the Ni-Mo/Al₂O₃ system was studied using the hydrogenation of naphthalene to tetraline at 300 or 350°C and 2.0 or 1.5 MPa as model reaction. The catalysts were either reduced or presulphided and the feed was either sulphur-free or contained small amount of benzothiophene. Two main conclusions are important for the theory of synergism in the hydrorefining catalysis: a) the Ni-Mo catalyst does not exhibit synergism in hydrodearomatization in the absence of sulphur in the system, b) in the presence of sulphur in the system, the synergism in hydrodearomatization occurs probably only under special conditions and is less general and less pronounced than in the hydrodesulphurization.

The synergism in the activity of bimetallic hydrorefining catalysts Ni-Mo and Co-Mo is an important phenomenon from both practical and theoretical point of view. It was studied predominantly in the hydrodesulphurization and the data for other hydrorefining reactions, hydrogenation of aromatic hydrocarbons, hydrodenitrogenation and hydrodeoxygenation are scarce¹. We believe that the comparison of the magnitude of the synergistic effect for various reactions and under various conditions is important for the elucidation of its mechanism.

The synergism in the activity for hydrogenation of unsaturated hydrocarbons can be studied both with sulphided and with unsulphided catalysts because the reactants do not contain sulphur. The synergism of the presulphided catalysts with the sulphur-containing feed was unambiguously proved for both the hydrogenation of olefins²⁻⁴ and the hydrogenation of aromatic hydrocarbons⁵⁻⁷. The magnitude of this effect for the hydrogenation of olefins is systematically lower than for the hydrodesulphurization¹; a reliable comparison for hydrodearomatization is not easy due to the lack of proper data in the literature.

The metallic Ni(Co) catalyst is very active in the hydrogenation of aromatic hydrocarbons but the presence of sulphur in the feed causes total deactivation of it⁸⁻¹¹. However, a direct comparison of the activities of the prerduced and of the presulphided catalysts with the sulphur-free feed has not been found in the literature. The metallic Mo catalyst is not very active in hydrodearomatization but it is also not sensitive to sulphur in the feed⁹.

The metallic Ni(Co)-Mo catalyst is quite active in the hydrodearomatization with the sulphur-free feed¹². The positive effect of presulphidation of this catalyst on the hydrodesulphurization activity is well known¹ but the situation in hydrodearomatization is less clear. A comparison of the reduced catalyst with the presulphided sample using sulphur-free feed is scarce in the literature; Yamada et al.^{13,14} reported that the sulphided sample was much more active than the reduced catalyst. The higher activity of the sulphided catalyst than of the reduced sample in the presence of sulphur in the feed is well described in the literature^{15,16}.

The aim of this work is to compare the magnitude of synergistic effect in the de-aromatization on Ni-Mo catalysts in the absence or presence of sulphur (sulphur introduced either before the reaction or during the reaction by the feed). The hydrogenation of naphthalene to tetrahydronaphthalene was chosen as the model reaction.

EXPERIMENTAL

Feed. The commercial naphthalene, even the grade puriss., contains usually benzothiophene; naphthalene supplied by Lachema (Brno, Czechoslovakia) and containing ca. 1% of benzothiophene was used in this work. It was fed into the reactor as the 16 mole % solution in pure decane (Fluka, 95%). Three solutions were prepared: purified solution (p) — totally desulphurized by the treatment with an excess of Raney nickel¹⁷ (50 g Ni per 1 l of the solution), partially purified solution (pp) — partially desulphurized by the same method (5 g Ni per 1 l of the solution) and nonpurified solution (np). Hydrogen was used without any purification.

Catalysts. Active components of the catalyst were supported on alumina Cherox 3300 (Chemical Works, Litvínov) which was crushed to the particle size fraction of 0.25–0.32 mm. The Ni-Mo, Ni and Mo catalysts contained 4% NiO + 12% MoO₃, 4% NiO and 12% MoO₃, respectively. The conventional method for catalysts preparation was used. The monometallic catalysts were prepared by drying in a rotating evaporator of the suspension of alumina in the solution of Ni(NO₃)₂·6 H₂O or (NH₄)₆Mo₇O₂₄·4 H₂O, followed by calcination in the stream of air at 400°C for 2 h. In case of bimetallic catalyst, the preparation consisted in impregnation of alumina by (NH₄)₆Mo₇O₂₄·4 H₂O, drying in a rotating evaporator at 80°C, impregnation by Ni(NO₃)₂·6 H₂O and calcination at 400°C for 2 h. The BET surface areas of all catalysts in the unsulphided state were ca. 125 m²/g. The presulphided catalysts were sulphided ex situ in H₂S/H₂ mixture at 350°C for 2 h.

Apparatus and procedure. Tubular pressure reactor (i.d. 3 mm) with the fixed catalyst bed was used. The solution of naphthalene in decane was fed into the reactor using a high-pressure pump. The feed rate of naphthalene and hydrogen was 0.013 and 0.27 mol h⁻¹, respectively. The liquid products of reaction were collected in a condenser at room temperature.

The catalysts were charged into the reactor either in the oxidic or presulphided state and were further activated in situ by the reduction in hydrogen stream (100 cm³ (STP) min⁻¹, 1 MPa). The temperature was increased to 400°C by the rate of 10°C min⁻¹ and was then kept constant for 30 min. The experimental conditions (300 and 350°C and pressure of 2.0 or 1.5 MPa) were set after activation. The samples of reaction mixture were taken in ten-minutes intervals into glass ampoules. They were analyzed by gas chromatography using a column filled with 20% Apiezon L/Rysorb BLK (Lachema, Brno, Czechoslovakia) and a TC detector.

Catalytic activity. The conversion of naphthalene was determined from the ratios of the peaks of naphthalene and decane in the feed and in the product. Practically no hydrogenation of tetraline to decaline was observed under conditions used.

RESULTS AND DISCUSSION

Sulphur influences the behaviour of the Ni, Mo and Ni-Mo catalysts in different manner. It is necessary to distinguish three situations: *a*) un sulphided catalyst and sulphur-free feed; *b*) un sulphided catalyst and sulphur-containing feed; *c*) pre-sulphided catalyst and sulphur-free feed.

Un sulphided catalysts and sulphur-free feed. The conversion was measured for various space times (W/F) at 300°C and 2.0 MPa and at 350°C and 1.5 MPa. The feed was purified solution (p). The results are shown in Fig. 1. The equilibrium conversions were calculated using literature data¹⁸.

The conversions for Ni and Ni-Mo catalysts at low W/F values were not stable with the time on stream t . This is probably caused by the deposition of coke in the catalyst bed. The deactivation was partially reversible and heating of the catalysts in pure hydrogen at 400°C for three hours restored 80–90% of the initial activity. However, the instability of conversion does not obstruct the comparison of the activity of the catalysts.

The activity of the Ni and Ni-Mo catalysts was comparable and high. Very low values of W/F had to be used to obtain conversions lower than the equilibrium

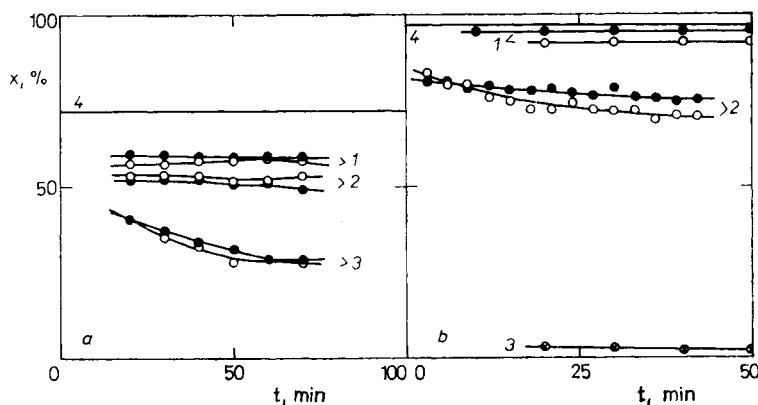


FIG. 1

Naphthalene conversion x versus time on stream t on un sulphided catalysts without sulphur in the feed (solution (p)). ● Ni-Mo, ○ Ni, ⊗ Mo. *a* Temperature 350°C, pressure 1.5 MPa. W/F , $g\ h\ mol^{-1}$: 1 27; 2 7.7; 3 0.8; 4 equilibrium conversion. *b* Temperature 300°C, pressure 2.0 MPa. W/F , $g\ h\ mol^{-1}$: 1 10; 2 1.5; 3 10; 4 equilibrium conversion

values. Also the rate of deactivation of both these catalysts was similar. On the other hand, the Mo catalyst was inactive; the conversion was small even at $W/F = 10 \text{ g h mol}^{-1}$.

It can be concluded that the activity of the Ni-Mo catalyst in the reduced form is caused by Ni and that Mo essentially does not contribute to it. The mixed Ni-Mo catalyst does not exhibit synergism in the hydrodearomatization in the absence of sulphur in the system. This finding cannot be compared with the literature data because no previous work has compared the hydrodearomatization activity of reduced Ni, Mo and Ni-Mo catalysts with the sulphur-free feed.

Unsulphided catalysts and sulphur-containing feed. The experiments were performed at 300°C and 2.0 MPa . The solutions (pp) and (np) were used as the feed and runs at several W/F were made. The results are shown in Fig. 2.

The data confirm the well known fact that the hydrogenation activity of a metallic Ni catalyst is strongly decreased by sulphur contained in the feed⁹⁻¹¹. The hydrodesulphurization of benzothiophene takes place simultaneously with the hydrogenation of naphthalene and hydrogen sulphide formed poisons gradually the catalytic bed. With the saturation of the bed by sulphur, the conversion dropped in several minutes from the equilibrium to zero conversion; this fact is in accord with literature data¹⁰. The fall in the activity in case of the solution (pp), containing less sulphur,

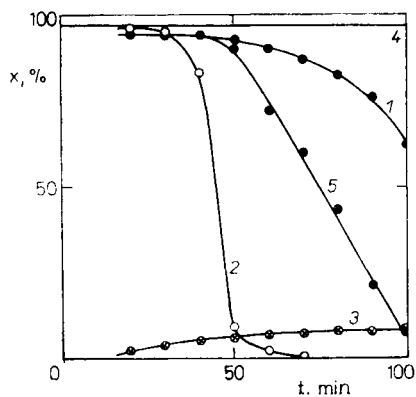


FIG. 2

Naphthalene conversion x versus time on stream t on sulphided catalysts with sulphur-containing feed. ● Ni-Mo, ○ Ni, ⊗ Mo. Temperature 300°C , pressure 2.0 MPa . W/F , g h mol^{-1} , solution (pp): 1 15; 2 25; 3 25; 4 equilibrium conversion. W/F , g h mol^{-1} , solution (np): 5 10

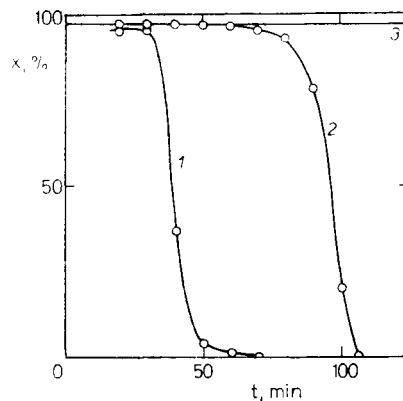


FIG. 3

Naphthalene conversion x versus time on stream t on unsulphided Ni catalyst with sulphur-containing feed. Temperature 300°C , pressure 2.0 MPa , $W/F = 55 \text{ g h mol}^{-1}$. 1 Solution (np); 2 solution (pp); 3 equilibrium conversion

occurred later than with the solution (np) (Fig. 3). It is important to point out that the character of the poisoning by sulphur (Figs 2, 3) is qualitatively different from the poisoning by coke observed in the experiments with the sulphur-free feed (Fig. 1).

The Mo catalyst had nearly zero initial activity but it was mildly activated by sulphidation in the course of the experiment (Fig. 2). Its activity after 100 min on stream was higher than the activity of the unsulphided Mo catalyst with the sulphur-free feed.

The Ni-Mo catalyst lost the activity very quickly, similarly as the Ni catalyst. However, its poisoning was not so quick as in the case of Ni. The higher resistance of the Ni-Mo catalyst against poisoning may be connected with higher number of centres able to bind sulphur; in the Ni-Mo catalyst sulphur attacks both Ni and Mo while in Ni catalyst only Ni. The poisoning of the Ni-Mo catalyst can also be mildly counterbalanced by increase of the Mo activity due to its sulphidation.

The areas under deactivation curves divided by W/F are proportional to the catalyst capacity for poison, i.e. to the amount of sulphur retained by one gram of catalyst. The ratio of these sulphur capacities for Ni-Mo and Ni catalysts was found to be approx. 5.6. This is close to the value 5.7 calculated from the metals content in the catalyst under the assumption of their full sulphidation to Ni_2S_3 and MoS_2 .

Sulphided catalysts and sulphur-free feed. The experiments were performed at 300°C and 2.0 MPa and at a single value of W/F . The results are presented in Fig. 4.

A stable activity of the catalysts was not achieved and the character of the $x-t$ curves was similar to that of reduced catalysts and sulphur-free feed. It is assumed that the decrease of activity is caused by the coke deposition on the surface.

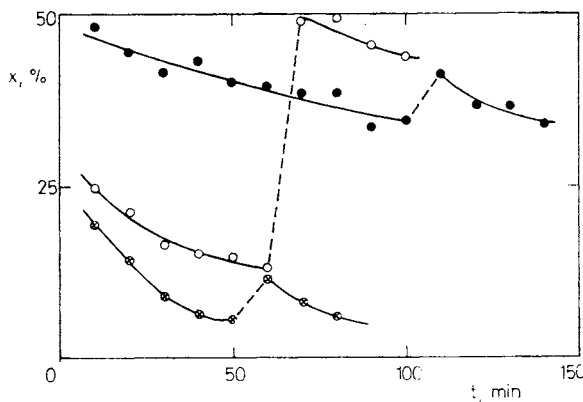


FIG. 4

Naphthalene conversion x versus time on stream t on sulphided catalysts without sulphur in the feed (dashed lines denote reduction at 400°C for 3 h). Temperature 300°C, pressure 2.0 MPa, $W/F = 22 \text{ g h mol}^{-1}$. ● Ni-Mo; ○ Ni; ⊗ Mo

The activity of sulphided Mo catalyst with the sulphur-free feed was comparable to the activity of reduced catalyst with the sulphur-containing feed (5% conversion at $t = 50$ min and $W/F = 22 \text{ g h mol}^{-1}$ in Fig. 4 and 6% conversion at $t = 50$ min and $W/F = 25 \text{ g h mol}^{-1}$ in Fig. 2).

However, the activity of the sulphided Ni and Ni-Mo catalysts with sulphur-free feed was considerable higher than the activity of the reduced catalysts with the sulphur-containing feed. E.g., the conversion over the Ni catalyst at $t = 60$ min and $W/F = 25 \text{ g h mol}^{-1}$ in Fig. 2 was almost zero, the conversion over it at the same t and $W/F = 22 \text{ g h mol}^{-1}$ in Fig. 4 was about 15%; similarly, for the Ni-Mo catalyst at 100 min and $W/F = 10 \text{ g h mol}^{-1}$ in Fig. 2 was $x = 5\%$ and at the same time at $W/F = 22 \text{ g h mol}^{-1}$ $x = 35\%$ in Fig. 4. This can be explained by the negative effect of hydrogen sulphide in the gas phase. With the reduced catalyst and sulphur-containing feed, the catalyst is firstly sulphided and the concentration of hydrogen sulphide in the gas phase is than kept stable by benzothiophene in the feed. With the presulphided catalyst and sulphur-free feed, the gas phase concentration of hydrogen sulphide is much lower because it is not supplied by the feed and the rate of desulphurization of the catalyst is low.

The initial conversions of the Ni-Mo catalyst in Fig. 4 ($x = 47\%$) is approximately equal to the sum of conversions of Ni ($x = 25\%$) and Mo ($x = 20\%$) catalysts, i.e. the fresh catalysts do not exhibit synergism. However, this picture changes with time on stream. The Ni-Mo catalyst deactivates more slowly than the Ni and Mo samples and the conversion on the Ni-Mo catalyst at $t = 50$ min in Fig. 4 is more then the sum of the conversions on the Ni and Mo catalysts; this effect cannot be denoted as synergism.

The additional reduction of the deactivated catalysts at 400°C for 3 h again changes the situation: this is shown in Fig. 4. The relation between the catalysts after this treatment is similar to that between the reduced catalysts in Fig. 1; the activities of Ni and Ni-Mo catalysts are comparable and high and the activity of Mo catalyst is low. The system also does not exhibit synergism in this state achieved by the additional reduction.

From experimental results of this work it can be concluded that the sulphur-free reduced catalyst, the reduced catalyst sulphided by the feed with low sulphur concentration and the sulphided catalyst presulphided by $\text{H}_2\text{S}/\text{H}_2$ do not exhibit synergism in hydrodearomatization.

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