HIGH ACTIVITY Ni-Mo/C HYDRODESULFURIZATION CATALYST: COMPARISON WITH COMMERCIAL Ni-Mo/Al₂O₃ CATALYST AT INCREASED HYDROGEN PRESSURE

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Hydrodesulfurization catalysts Ni-Mo/C were prepared using active carbon extracted by various solvents. A special feature of the comparison with conventional alumina-supported catalyst was the use of increased hydrogen pressure of 1.6 MPa and the utilization of a commercial Ni-Mo/Al₂O₃ sample. The best Ni-Mo/C catalyst was 3.6 times more active than the Ni-Mo/Al₂O₃ reference catalyst. Therefore, better performance of carbon-supported sulfides is not limited to the region of low pressure as suggested by some previous authors.

1. Introduction

Carbon-supported Co-Mo and Ni-Mo sulfides are considered to be more active hydrodesulfurization catalysts than the corresponding alumina-supported sulfides [1–5]. However, the attainable level of the activity of carbon-supported catalysts and the difference in the activity between carbon- and alumina-supported catalysts have not been fully evaluated in two respects: (i) almost all previous comparative studies tested activity at atmospheric pressure [6–11], and (ii) they often used only laboratory-made samples of alumina-supported catalysts [8–10].

At atmospheric pressure, the coking of alumina-supported catalysts is intensive, while the coking propensity of carbon-supported catalysts is low [3,10]. The coking of alumina-supported catalysts is known to be prevented by increased hydrogen pressure. It was suggested that the difference in activity between carbon- and alumina-supported sulfides is limited to low hydrogen pressure and that this difference disappears at increased pressure [3]. However, the published activity data measured at increased pressure are very scarce. Groot et al. [3] observed higher activity for a Co-Mo/C sample than for a Co-Mo/Al₂O₃ catalyst at a pressure of 3.5 MPa, while the order of activity at 7.0 MPa was just opposite.

Startsev et al. [4] found that the activity ratio of carbon- and laboratory-made alumina-supported Ni-Mo catalysts was 2.2 at a pressure of 2 MPa. It is concluded that more data, measured at increased pressure, is needed.

A generally recognized standard hydrodesulfurization catalyst has not been established. The activities of laboratory-made alumina-supported catalysts might vary in a broad range and so a comparison does not give unambiguous information on the activity levels of carbon-supported samples. Commercial alumina-supported catalysts are more suitable for reference points because their activities are optimized and they are readily available. However, the few previous comparative studies which included commercial catalysts were performed at atmospheric pressure [6,7,11].

The purpose of the present work was to evaluate the activities of Ni-Mo/C and commercial Ni-Mo/Al_2O_3 catalysts at increased hydrogen pressure.

2. Experimental

The active carbon was GA-1, produced by Slovenské lučobné závody, Hnúšta, Czechoslovakia. It is a microporous, high surface area material containing potassium hydroxide as additive. It was crushed to the particle size fraction of 0.16–0.32 mm and portions of it were purified by sequential extraction by various solvents. The supports obtained were denoted as C(1) to C(5), as summarized in table 1. After the extraction with the last solvent shown in table 1, the samples C(3), C(4) and C(5) were washed with ethanol and water. The texture of sample C(2) was characterized by nitrogen adsorption measured using Digisorb 2600 apparatus (Micromeritics), the BET surface area was 1100 m^2g^{-1}, the pore volume at saturation was 0.75 cm^3g^{-1}, the volume of the micropores with radius smaller than 1 nm was 0.49 cm^3g^{-1}.

Table 1
Hydrodesulfurization activity of Ni-Mo/C catalysts normalized to the reference Ni-Mo/Al_2O_3 Shell 324 catalyst

Catalyst	Solvents [a]	$k(j)/k(r)$ [b]
Ni-Mo/C(1)	none	0.3
Ni-Mo/C(2)	water	3.1
Ni-Mo/C(2,sim)	water	0.6
Ni-Mo/C(3)	water, n-butanol	3.2
Ni-Mo/C(4)	water, n-butanol, dimethyl-sulfoxide	3.6
Ni-Mo/C(5)	water, n-butanol, toluene	2.3

[a] Sequential extraction of the carrier GA-1 at the boiling point of the solvent.
[b] $(k(j)/k(r)) = 1$ for Ni-Mo/Al_2O_3 catalyst.

The Ni-Mo/C catalysts contained 12 wt.% MoO_3 and 3 wt.% NiO. The Ni-Mo/C(i) samples were prepared by conventional sequential impregnation (Mo first) using aqueous solutions of $(NH_4)_2Mo_7O_{24}.4H_2O$ and $Ni(NO_3)_2.6H_2O$. The Ni-Mo/C(2,sim) sample was prepared by simultaneous impregnation of both metal salts the by pore filling method. The impregnation solution was obtained by mixing cold solutions containing 0.25 g ml^{-1} and 0.2 g ml^{-1} of $(NH_4)_2Mo_7O_{24}.4H_2O$ and $Ni(NO_3)_2.6H_2O$, respectively. All samples were dried at 100°C in a vacuum rotary evaporator after each impregnation step and were not calcined.

The commercial Ni-Mo/Al$_2$O$_3$ reference sample was the Shell 324 catalyst and contained 17.7 wt.% MoO_3 and 3.4 wt.% NiO. It was crushed to a particle size fraction of 0.16–0.32 mm. The catalyst surface area was 160 m^{2}g^{-1}, the pore volume at saturation was 0.44 cm^{3}g^{-1} and the micropore volume was negligible.

The catalyst activity in the hydrodesulfurization of thiophene, TH, was measured in a fixed bed flow reactor (I.D. = 2.5 mm). The total pressure was 1.6 MPa, the initial partial pressure of TH was 40 Pa, the feed rate, F(TH), was 0.6 mmol h^{-1}, the hydrogen flow was 1.5 mol h^{-1}, and the catalyst charge, W, was always 0.01 g. The catalyst was in-situ, presulfided with a H_2S/H_2 mixture (1 : 10) at atmospheric pressure of 400°C for 2 h. The feed was introduced at the pressure of 1.6 MPa and the conversion of TH, x(TH), was sequentially determined at several temperatures from 400 to 200°C, changing the temperature in steps of 20°C.

3. Results and discussion

In the hydrodesulfurization of thiophene at atmospheric hydrogen pressure, considerable deactivation of the catalysts occurs in the initial period of the run [8,12]. No deactivation was observed in our experiments at the hydrogen pressure of 1.6 MPa. We believe that the activities of catalysts obtained in the present work are not affected by the coke formation on the surface.

The typical dependences of x(TH) on temperature are shown in fig. 1. The important result was that the curves did not cross. Our previous experience with various catalysts showed that under the conditions of our test (fixed pressure, initial concentration of TH and F(TH)), the dependence x(TH) $= f(W/F$(TH)) in the range of x(TH) from 0.01 to 0.90 follows the pseudo-first order equation

$$\ln(1 - x(\text{TH}, j)) = \frac{k(j)}{k(r)}\ln(1 - x(\text{TH}, r))$$ (1)

with rate constant k. Eq. (1) can be written for each temperature, where j and r denote the j-th and the reference Ni-Mo/Al$_2$O$_3$ catalyst, respectively. Straight lines were obtained by plotting conversions x(TH) at various temperatures according to eq. (1). This is illustrated in fig. 2. The ratios $k(j)/k(i)$ obtained
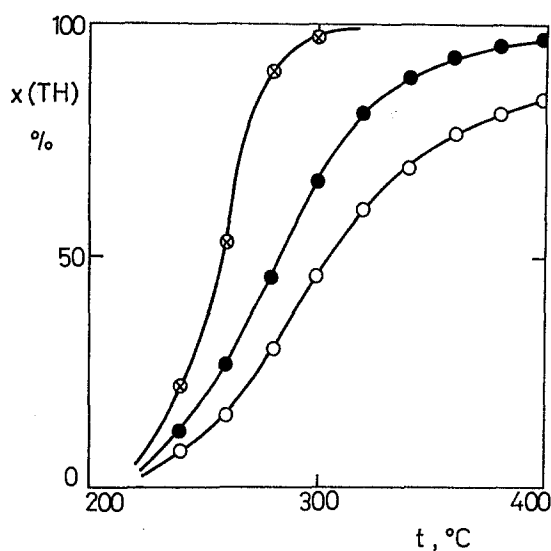
Fig. 1. The dependence of the conversion of thiophene on temperature. ⊗ Ni-Mo/C(3), ● Ni-Mo/Al₃O₃, Shell 324, ○ Ni-Mo/C(2,sim).

are the parameters independent of temperature and are shown in table 1. They are well applicable for the evaluation of the relative activity of the catalysts in the whole range of temperatures used. However, they were derived from the narrow range of kinetic variables, their physical meaning is only formal and they are not suited to make meaningful conclusions regarding activation energies.
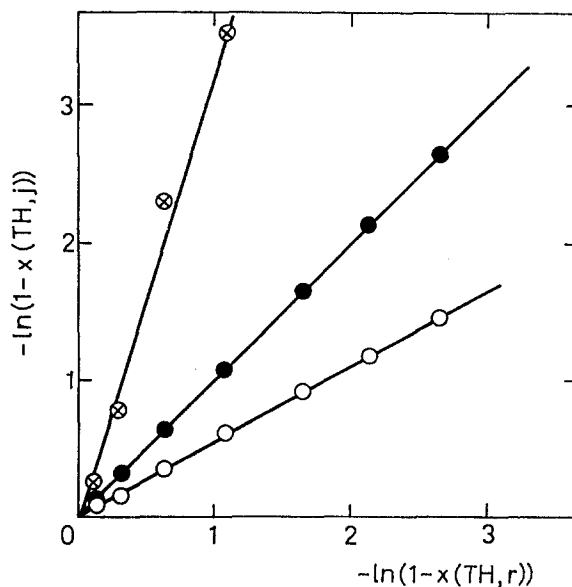

Fig. 2. The illustration of validity of eq. (1); symbols have the same meaning as in fig. 1.

It is seen from table 1 that purification of the carrier by extraction with water greatly improved the activity of the catalyst. Additional small activity increases were achieved by the extraction with n-butanol and dimethylsulfoxide, respectively. On the other hand, the additional treatment with toluene had a negative effect. Toluene was probably strongly adsorbed, was not removed by washing with ethanol and water, and increased the hydrophobicity of the carrier.

The catalyst prepared by simultaneous impregnation, Ni-Mo/C(2,sim) was much less active than the catalyst Ni-Mo/C(2) prepared by consecutive impregnation. This agrees with the results of Daly et al. [7], while Startsev et al. [4] observed the opposite. It seems that the impregnation procedure deserves more systematic study to optimize the catalyst activity.

The best Ni-Mo/C catalyst in table 1 was almost four times more active than the reference Ni-Mo/Al_2O_3 catalyst, which moreover contained more active metals. Our data thus show that the higher activity of carbon- than of alumina-supported catalysts is not connected with the region of low hdyrogen pressure. It is important that this result was obtained by comparison with high activity, commercial Ni-Mo/Al_2O_3 catalyst.

It seems that the difference in activity between carbon- and alumina-supported catalysts is not connected with the different coking propensities of these catalysts. This conclusion agrees with the results of van Veen et al. [9] who studied alumina-, silica- and carbon-supported catalysts and found that the nature of the support influences the intrinsic specific activity of the active CoMoS phase.

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