PREPARATION AND EVALUATION OF SKELETAL COBALT–MOLYBDENUM HYDRODESULFURIZATION CATALYSTS

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Preparation of skeletal Co–Mo catalysts by controlled impregnation of aluminosilicate skeletons containing deposited gamma-alumina with aqueous solutions of active component precursors has been investigated. The activity of the laboratory catalysts in gas oil hydrodesulfurization has been determined. Kinetics of impregnation of skeletal supports, the effect of their type, and the dependence of catalyst activity on the content of cobalt and molybdenum sulfides are reported. HDS skeletal catalysts prepared were compared with the extruded types. It was found that skeletal HDS catalysts show the higher activity (related to the content of alumina and Co–Mo sulfides) than the extruded ones due to the less significant effect of internal diffusion. However, if the activity is related to the same volume of catalyst bed, the activity of skeletal catalysts is only one fourth of that of the extruded types.

Hydrodesulfurization is of continuous importance in oil cuts processing, especially with regard to ecological aspects. At present, industrial catalysts are mostly the extruded or pelleted types. The effects of the shape of catalyst particles and their dimensions on gas oil hydrodesulfurization were studied in our previous work[1]. The rate of this reaction was found to be considerably affected by diffusion transport of reactants through the porous structure of the catalyst particle. One way how to take away or to reduce the effect of transport phenomena on the catalytic process is the use of monolitic or skeletal catalysts. These possess usually a nonporous ceramic matrix with multiplex oriented or nonarranged channels, the walls of which are lined with a thin layer of the catalytically active mass. These catalysts have found wide use not only in gas phase reactions (e.g. after-oxidation of flue gases) but recently also in multiphase reaction systems[2,3]. Thus, for example, EKA-Nobel company operates a unit in which a monolitic reactor is used in the hydrogenation step of alkyl anthraquinone process for the hydrogen peroxide production[4]. Comparison of the monolitic reactor with the trickle-bed one for liquid phase hydrogenations has been recently reported[5]. Major differences between both reactors consist in the different geometry of the catalyst which affects its amount in the reaction space, the resistance against external and internal mass transport, the interface area as well as the pressure drop.

The present work is concerned with the evaluation of the applicability of skeletal catalysts to gas oil hydrodesulfurization. Their activity is compared with that of conventional industrial catalysts used in the form of the extrudates.

EXPERIMENTAL

Chemicals and Catalysts

Cobalt(II) nitrate hexahydrate, analytical grade, ammonium heptamolybdenate tetrahydrate, analytical grade, were supplied by Lachema Brno. Sulfan was purchased from Merck–Schuchardt. Hydrogen, electrolytic, was obtained from Linde-Technoplyn Prague, crude gas oil (Chemopetrol Litvínov) contained 0.95 wt.% sulfur and 50 wt.% aromatic hydrocarbons and had the initial boiling point 166 °C (50% of the oil distilled at 272 °C and 90% at 350 °C).

Three types of skeletal supports with deposited gamma-alumina used in this work were designated as A, B, and C. The supports had cylindrical shape (diameter × height = 40 × 12 mm). The skeletons were supplied by Chemopetrol Litvínov and the gamma-alumina deposition was performed in Institute of Chemical Process Fundamentals, the Academy of Sciences of the Czech Republic, Prague. Type A was the support with a porous cylinder shell, types B and C had a nonporous cylinder shell and differed from each other by the number of holes per length unit (ppi). Characteristics of the skeletons used is presented in Table I. It is evident that the free volume of skeletons amounts to two thirds of the total skeleton volumes, and further the types used in the present work do not show any significant difference, when compared to each other. The thickness of the deposited alumina layer was ca 0.2 mm.

Preparation of Co–Mo Catalyst

Skeletal supports of the catalyst were impregnated with aqueous solutions of the active component precursors until equilibrium establishment. The support was first impregnated with a solution of ammonium heptamolybdate, and after drying and calcination, it was impregnated with cobalt(II) nitrate solution.

The skeletal support was immersed into 50 ml of ammonium molybdate solution of the known concentration, and then air in the pores of gamma-alumina was taken away under vacuum (5 min). The impregnation proper was carried out at 25 °C for 2 h with stirring the impregnating solution. At fixed time intervals, the samples of the solution were withdrawn and analyzed. The amount of the active component adsorbed on the support was determined from its concentration decrease in the

TABLE I
Characteristics of skeletal supports

Type	V_{sk}, cm^3	V_{free}, cm^3	V_{free}/V_{sk}, %	ppi[a]
A	12.9	8.4	65	10
B	15.1	10.1	67	15
C	17.2	11.7	68	20

[a] Number of holes per inch.

impregnating solution. After the equilibrium had been attained (i.e. the concentration of a given component in the solution remained practically constant), the catalyst was withdrawn and dried at ambient temperature for 15 min and then in air at 120 °C for another 2 h. The dry catalyst was calcined in air at 450 °C for 7 h. In subsequent impregnation, after the first saturation, the calcined catalyst was saturated with the second active component (with cobalt(II) nitrate).

All the catalysts were sulfided prior to their use with a mixture of hydrogen (95 vol.%, flow rate 15 l h^{-1}) and sulfan (5 vol.%, flow rate 0.8 l h^{-1}) at atmospheric pressure and 350 °C for 8 h.

Catalyst Activity Measurements

The activity of prepared catalysts was measured in a stirred isothermal autoclave with a stationary bed of catalyst. The equipment was discontinuous with respect to the catalyst and raw material and continuous with respect to hydrogen because of the removal of the formed sulfan from the reaction mixture. The autoclave and procedure were described in detail elsewhere[6].

The hydrodesulfurization activity of prepared catalysts was measured under following conditions: reaction temperature 300 °C, hydrogen overpressure 3 MPa, reaction time 4 h, outgas flow rate 15 l h^{-1}, initial volume of the raw material (gas oil) 200 ml, stirrer revolution 1 500 min^{-1}, skeletal catalyst weight 7 – 16 g, extruded catalyst weight 5 g.

Analytical Methods

The course of the support saturation by the active components was followed by measuring the metal content decrease in the impregnating solution. At fixed time intervals, the samples were withdrawn and analyzed spectrophotometrically.

Photometric determination of molybdenum by potassium thiocyanate[7,8]. In an acid medium (sulfuric acid), molybdenum reacts with potassium thiocyanate in the presence of ascorbic acid to form an orange to red complex. The intensity of the complex colouring becomes constant only after 35 min. The maximum molybdenum content in the analytical sample is 4 mg per liter, and photometric determination is carried out at 440 nm. The presence of cobalt does not interfere the measurement.

Photometric determination of cobalt by 4-(2-pyridylazo)resorcinol[7,9]. Cobalt(II) ions react with the resorcinol (PAR) in neutral or weakly basic media (pH 6 – 9) to give a red, water soluble complex. The complex is formed at a fast rate and is stable for 24 h. The analytical sample should contain 0.1 to 1 mg cobalt per liter. Photometric determination is carried out at 510 nm. The presence of molybdenum does not interfere the measurement.

Determination of sulfur content. The method used consists in combustion of sulfur-containing compounds[10] contained in the sample in oxygen atmosphere to form sulfur dioxide which is then oxidized by hydrogen peroxide to sulfuric acid. The acid is titrated with barium perchlorate, using Thorin I and Methylene Blue as indicators[11].

RESULTS AND DISCUSSION

Kinetics of Impregnation

We have first examined kinetics of the impregnation of skeletal catalysts by the precursors of the active components, i.e. of cobalt and molybdenum. The example of the two-step impregnation of gamma-alumina on skeleton C, first by ammonium heptamolybdate and then, after its drying and calcination, by cobalt(II) nitrate is shown

in Fig. 1. It is seen that the decrease in the molybdenum concentration in the impregnating solution is higher than in the case of cobalt, even though the initial molybdenum concentration is lower than the cobalt concentration. One can also state that the adsorption equilibrium is established in 50 min. These results were compared with previous data[12] on kinetics of impregnation of extruded catalysts. In that case the authors used the extruded alumina of the chloride type, with particles having 1.74 mm diameter and 7.5 mm medium length. Comparison of the impregnation of the gamma-alumina deposited on the skeleton with the extruded catalyst support is made in Table II. It is evident that the time required to achieve equilibrium is six times longer for the extruded form of the alumina than that for the skeletal support, since in the case of the skeletal support with a thin layer of gamma-alumina, the effect of internal mass transport is strongly supressed when compared to the extruded support.

Adsorption Equilibrium

Further measurements concerned with adsorption equilibria of the components for different initial concentrations of their precursors in the impregnating solution. The

TABLE II
Impregnation of skeletal and extruded catalyst support (temperature 25 °C)

Catalyst	w_{cat}, g	V_{sol}, l	w_{cat}/V_{sol}, g l^{-1}	t^a, min
Skeleton C	0.83	0.05	16.6	50
Extruded	12.00	0.30	40.0	300

[a] Time of equilibrium attainment.

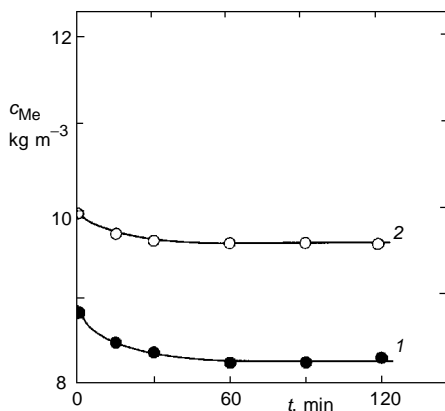

FIG. 1
Time dependence of molybdenum or cobalt concentration in impregnating solution in two-step saturation of skeletal support C. Sequence: $[(NH_4)_6Mo_7O_{24} . 4 H_2O]$, then $[Co(NO_3)_2 . 6 H_2O]$, skeleton weight 10.4155 g, gamma-alumina weight 0.8301 g; *1* molybdenum; *2* cobalt

measurements were aimed at a quantitative description of the effect of the initial concentration of the impregnating solution on the amount of deposited active component precursor. For this purpose we used the skeleton C which was cut into four parts. Individual parts of the support were impregnated such that the gamma-alumina weight to impregnating solution volume was maintained the same. The impregnation was carried out by using different initial concentrations of the active component precursors at 25 °C for 2 h. In all experiments, the air within the support pores was first taken away by evacuation of the support immersed in the impregnating solution. In the first stage, the pure gamma-alumina surface of skeleton C was treated with ammonium heptamolybdate. In the case of the cobalt adsorption, the pure skeleton C was impregnated as a whole first by molybdenum, then it was dried and calcinated (MoO_3 concentration 13.2 wt.%), cut into four parts, and then impregnated with cobalt(II) nitrate solutions of different initial concentrations under identical conditions as in the case of molybdenum.

Experimental data were treated by means of the adsorption isotherm, using here the Freundlich relation (*1*).

$$c_a = K c_e^n \tag{1}$$

The linearized Freundlich relation was used to obtain the values of adsorption constants. In Fig. 2, the results of these measurements are shown in the form of the linearized Freundlich relation. From these dependences, the following relations were obtained for

$$\text{molybdenum} \quad c_a = 5.78 \; c_e^{1.24} \tag{2}$$

and

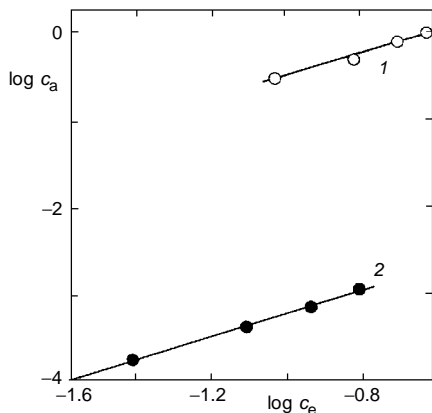$$\text{cobalt} \quad c_a = 0.014 \; c_e^{1.33} \; . \tag{3}$$

Fig. 2
Linearized Freundlich adsorption isotherm (for skeletal support C), temperature 25 °C; *1* molybdenum, *2* cobalt

Correlation coefficients for Eqs (*2*) and (*3*) were 0.988 and 0.998, respectively. Based on these relations, the initial concentrations of the active component precursors were chosen in preparing HDS skeletal catalysts of a given composition. The values of adsorption constants show unambiguously that molybdenum is adsorbed on the starting gamma-alumina distinctly more strongly than is the cobalt on the gamma-alumina containing already molybdenum. With regard to similar characteristics of all the skeletons used, the above mentioned relations were applied with success also in preparing the catalysts on skeletons A and B.

Hydrodesulfurization Activity of Co–Mo Catalysts

Time dependence of sulfur content in gas oil hydrodesulfurization determined for the skeletal HDS catalyst is shown in Fig. 3. The reaction is first order in the sulfur content in the reaction mixture. This is documented by data in logarithmic coordinates for the first order which were modified by the change of reaction mixture volume due to a regular withdrawal of the samples from the autoclave[10]. From the slopes of these dependences, determined with the use of linear regression, the rate constants of hydrodesulfurization were obtained. These are considered to be the measure of the catalyst activity. The same procedure was used to evaluate the activity of the extruded catalyst.

Comparison of the activity of the skeletal with extruded catalyst is shown in Table III. Compared were four catalysts prepared in the same way (i.e. by two-step impregnation including the impregnation by molybdenum in the first step, followed, after sample drying and calcination, by the cobalt impregnation in the second step). The catalysts contained comparable amount of the active components, and were calcinated and sulfided under identical conditions. The activities of these catalysts are related to the weight of the active catalyst (gamma-alumina – molybdenum(IV) sulfide – cobalt(II)
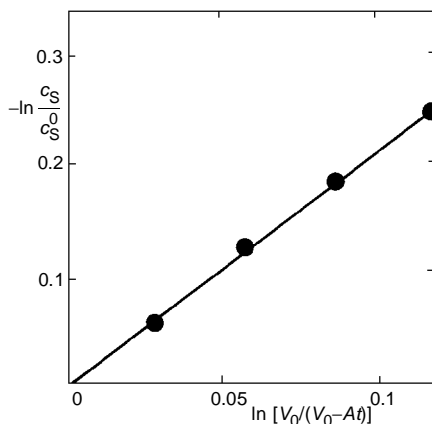

FIG. 3
Time dependence of the degree of gas oil desulfurization in the form of first order coordinates (300 °C, 3 MPa, $V_0 = 0.2$ l, $A = 7.5$ ml h^{-1})

sulfide). One can state that the skeletal HDS catalysts show higher activity, related to the content of the gamma-alumina and sulfides. This may be ascribed to the fact that these catalysts are affected less by internal diffusion which results from a thin layer of the active catalyst in the case of the skeletal type. However, if the activity is related to the skeleton volume or to the same volume of the catalyst bed (the so defined activity expresses the space productivity of a given equipment), the activity of the skeletal catalysts amounts to only 15 – 27% (in dependence on the free skeleton volume) of that of the extruded catalyst.

In the present work a total of 20 samples of skeletal catalysts containing different amounts of the active components have been compared. The comparison showed that the activity of these catalysts can be directly related to the total content of molybdenum and cobalt sulfides, as documented in Fig. 4. At the same time, the activity of prepared catalysts has not been affected by the type of the skeleton used (A, B, C).

TABLE III
Comparison of skeletal and extruded HDS catalyst (300 °C, 3 MPA, A = 7.5 ml h^{-1})

Catalyst	MoO$_3$, wt.%	CoO, wt.%	k_a . 10^5	k_b . 10^2
Skeleton A	14.8	3.6	5.56	0.696
Skeleton B	15.4	4.1	5.88	0.432
Skeleton C	13.4	4.2	5.77	0.387
Extruded	15.0	3.5	4.99	2.57

Rate constant of hydrodesulfurization k_a related to catalyst weight; rate constant of hydrodesulfurization k_b related to catalyst volume.
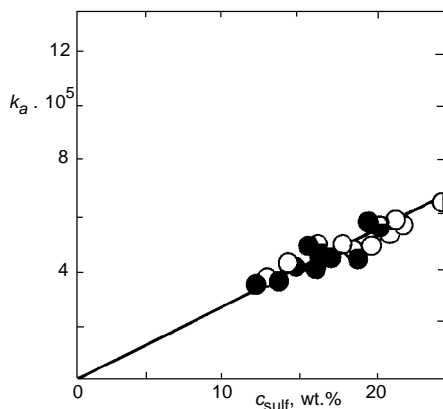

FIG. 4
Dependence of catalyst activity on content of sulfides (c_{sulf}) for individual types of skeletal supports (300 °C, 3 MPa, V_0 = 0.2 l, A = 7.5 ml h^{-1}). ○ Skeleton A, ◐ skeleton B, and ● skeleton C

Summarizing, the skeletal HDS catalysts do not seem to be capable of replacing the extruded types as their volume activity is markedly lower. However, their application could be of advantage due to the low pressure drop, high thermal stability, and favourable selectivity (resulting from a thin layer of the active catalyst). They can serve especially as flow distributors in trickle-bed reactors.

SYMBOLS

A	rate of decrease of reaction mixture volume caused by withdrawal of samples for analysis, ml h^{-1}
c_a	concentration of the adsorbed component, mol kg$_{cat}^{-1}$
c_e	equilibrium concentration of a given component in impregnating solution, mol l^{-1}
c_S^0	initial sulfur concentration in liquid sample, wt.%
c_S	sulfur concentration in liquid sample at time t, wt.%
c_{Me}	concentration of a metal (Co or Mo), kg m^{-3}
c_{sulf}	concentration of Mo and Co sulfides on catalyst, wt.%
k_a	rate constant of hydrodesulfurization related to catalyst weight, dm^3 min^{-1} kg$_{cat}^{-1}$ kPa^{-1}
k_b	rate constant of hydrodesulfurization related to catalyst volume, dm^3 min^{-1} m$_{cat}^{-3}$ kPa^{-1}
K	adsorption constant
n	exponent in Eq. (*1*)
t	time, min
V_0	initial volume of reaction mixture, ml
V_{sol}	initial volume of impregnating solution, l
V_{sk}	geometrical volume of skeleton, cm^3
V_{free}	free volume of support channels, cm^3
w_{cat}	weight of catalyst support (gamma-alumina), g

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