

## DEVELOPMENT OF COBALT-MOLYBDENUM HYDRODESULFURIZATION CATALYSTS

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*Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.*

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The Co-Mo catalysts have been prepared on laboratory scale by controlled impregnation of extruded  $\gamma$ -alumina with aqueous solutions of suitable active components, and their activity has been tested in the hydrodesulfurization and hydrogenation of aromatic compounds in gas oil. The kinetics of impregnation of the carrier, the effect of its nature, the order of impregnation of precursors of the individual active components, and the effect of their nature on the activity of the catalyst prepared have been studied. The samples prepared have been compared with selected commercial catalysts.

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The hydrorefining operations are constantly important for the treatment of crude oil fractions, particularly with regard to ecological aspects. One of the first monographs devoted to the preparation and properties of sulfidic catalysts for use in these processes was published by Weisser and Landa<sup>1</sup>. A recent review article by Zdražil<sup>2</sup> summarizes the findings concerning the preparation, properties, and applications of the said catalysts to hydrogenation and hydrorefining processes. Moreover, the effect of composition of the catalyst on the hydrodesulfurization mechanism was presented in an extensive report by Zdražil and Kraus<sup>3</sup>. Most hydrorefining catalysts are prepared by the impregnation procedure followed by calcination and sulfidation. A survey of factors affecting the impregnation can be found, e.g. in refs<sup>4,5</sup>.

The present communication is a continuation of our earlier efforts to develop an original method of preparation and activity evaluation of hydrodesulfurization catalysts based on cobalt and molybdenum<sup>6</sup>. Our earlier reports<sup>7,8</sup> dealt with measurements of adsorption equilibria of precursors of the active components on the  $\gamma$ -alumina carrier and with a model of impregnation of catalyst particles enabling a prediction of concentration profiles of components in the particle. The evaluation of activity of hydrodesulfurization catalysts based on the application of the autoclave designed by Berty<sup>9</sup> was developed in another paper<sup>10</sup>.

## EXPERIMENTAL

### Reagents and Catalysts

Cobalt(II) nitrate hexahydrate (p.a.), cobalt(II) chloride hexahydrate (p.a.), cobalt(II) formate dihydrate (pure), ammonium heptamolybdate tetrahydrate (p.a.), 25% aqueous ammonia (p.a.), all from Lachema Brno. Hexaamminecobalt(II) chloride was synthesized by a reaction of cobalt(II) chloride and ammonia in the molar ratio of 1 : 3. Electrolytical hydrogen and nitrogen from Technoplyn Prague. Raw gas oil containing 0.98% sulfur, 25% aromatic compounds, beginning of boiling at 166 °C, 50% is distilled at 272 °C, 90% at 350 °C.

Three types of  $\gamma$ -alumina (denoted as A, B, C) were used as the carrier. The individual types differ in the starting materials, way of preparation, final composition, and properties. The type A (Pural SB) is an alkoxide alumina (cylindrical extrudates of 1.7 mm diameter) prepared from the aluminium(III) hydroxide obtained by hydrolysis of the alkoxides in Alfol Process (Condea, Germany). The type B is an aluminate alumina (Cherox 33-00), cylindrical extrudates of 1.8 mm diameter (Chemopetrol CHZ Litvínov). The chloride type C has been developed on laboratory scale on the basis of aluminium(III) chloride, cylindrical extrudates of 1.75 mm diameter (VÚCHVU CHZ Litvínov).

Before the activity tests, the commercial catalysts Shell 344 (2.36% Co, 9.17% Mo, extrudates of 1.53 mm diameter, Shell Holland), KF 702 (2.85% Co, 8.59% Mo, extrudates of 1.36 mm diameter, AKZO Chemie Holland), and Cherox 36-01 (2.75% Co, 9.10% Mo, Chemopetrol CHZ Litvínov) were calcinated and sulfurized in the same way as the catalysts prepared by us.

### Preparation of Catalysts

The catalyst carriers were impregnated with aqueous solutions of precursors of the active components until establishing the equilibrium. Three types of catalysts were prepared. The types MC and CM were obtained by the method of subsequent impregnations of the carrier starting with the solutions of ammonium molybdate and cobalt salt, respectively. After drying and calcination, the respective second active component was then impregnated. The type Z denotes the procedure of competition impregnation, the impregnation solution containing both active components at the same time. The air present in the pores of the carrier was removed by evacuation under water for 10 min. The impregnation itself was carried out at 25 °C in an agitated vessel<sup>11</sup> with a stationary layer of the carrier. At regular intervals, samples of the impregnation solution were taken and analyzed. From the concentration decrease the amount of the active component adsorbed on the carrier was estimated. After reaching the equilibrium (the concentration decrease of the solution stopped), the catalyst was taken out from the impregnation apparatus and dried in a vacuum rotary evaporator at 1.3 kPa at 60 °C for 2 h. The dry catalyst (30 g) was calcinated in a stream of nitrogen (20 dm<sup>3</sup> h<sup>-1</sup>) at 450 °C for 7 h. Then in the second impregnation, the calcinated catalyst was saturated with the solution of the other active component. Before the application proper, all the catalysts – both the synthesized and commercial ones – were sulfurized with a 5% solution of dimethyl disulfide in cyclohexane in a stream of hydrogen (0.66 dm<sup>3</sup> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) at 340 °C at atmospheric pressure 7 h.

### Catalyst Activity Measurements

The activity of the catalysts prepared was measured in a stirred isothermal autoclave with a stationary level of the nonground catalyst. This apparatus was discontinuous with respect to the catalyst and the material treated and continuous with respect to the hydrogen used for removing the hydrogen sulfide formed from the reaction mixture. The apparatus and procedure are described in detail elsewhere<sup>10</sup>. The hydrodesulfurization activity of the catalysts was measured at the following reaction conditions: the temperature

of 300 °C, the hydrogen pressure of 3 MPa, the reaction time of 4 h, the relief gas flow rate of 15 dm<sup>3</sup> h<sup>-1</sup>; the starting volume of gas oil was 200 ml, the catalyst weight was 5 g.

#### Analytical Methods

The course of saturation of the carrier with the active components was monitored by means of the decrease in the metal concentration of the impregnation solution. At definite time intervals samples were taken and analyzed spectrophotometrically.

*Determination of molybdenum with potassium thiocyanate.* Molybdenum forms an orange to red complex with potassium thiocyanate in acid medium (sulfuric acid) in the presence of ascorbic acid<sup>12,13</sup>. The intensity of colouration of the complex is not stable until after 35 min. The maximum content of molybdenum in a sample measured can be 200 µg per 50 ml, the photometry being carried out at the wavelength of 440 nm. The presence of cobalt does not interfere with the determination.

*Determination of cobalt with 4-(2-pyridylazo)resorcinol.* Cobalt(II) ion forms an orange-red water-soluble complex with 4-(2-pyridylazo)resorcinol (PAR) in neutral to slightly alkaline media (pH 6 to 9)<sup>12,14</sup>. The complex is formed very rapidly and is stable for 24 h. The sample analyzed must contain from 5 to 50 µg cobalt per 50 ml. The photometry is carried out at 510 nm. The presence of molybdenum does not interfere with the analysis.

*Determination of sulfur content.* The method adopted is based on the combustion of the sulfur-containing compounds<sup>15</sup> present in the sample in air atmosphere to give sulfur dioxide which is then oxidized with hydrogen peroxide to sulfuric acid. The acid is determined titrimetrically with barium(II) chloride using the photometric indication.

## RESULTS AND DISCUSSION

### *Impregnation Kinetics*

The first research phase of preparation of the hydrodesulfurization catalysts based on cobalt and molybdenum was focused on the impregnation kinetics of  $\gamma$ -alumina type B with aqueous solutions of cobalt compounds. An example of time course of concentration of various cobalt compounds in the impregnation solution during saturation of the said carrier in an discontinuous arrangement is presented in Fig. 1. The experiments were carried out at room temperature, and the ratio of the carrier weight to the impregnation solution volume was 0.05 kg dm<sup>-3</sup>. The results clearly show the difference in the rate of reaching the steady state in the system carrier-impregnation solution, as well as the difference in the final decrease of cobalt compound in the solution. Table I gives the time needed for attaining the steady state and the final equilibrium concentration of cobalt(II) oxide on the catalyst. As it follows from these data the CoO content in the catalyst increases with increasing pH value of the impregnation solution. The highest equilibrium concentration was found for ammoniacal solution of hexaamminecobalt(II) chloride. Of course, the time needed to attain the steady state increases with increasing content of the impregnated component.

In the next research phase we studied the simultaneous impregnation of cobalt and molybdenum compounds on various samples of  $\gamma$ -alumina (three samples of various

provenience). The time courses of cobalt(II) nitrate and ammonium molybdate concentrations in the impregnation solutions are presented in Figs 2 and 3, respectively. It can be seen that the character of carrier affects the impregnations of the cobalt salt and the molybdenum salt in the same way. The highest equilibrium content of the two

TABLE I  
Effect of nature of cobalt compound on equilibrium concentration of CoO on  $\gamma$ -alumina B ( $T = 298$  K, initial cobalt concentration in solution  $C_0 = 3.19$  kg m<sup>-3</sup>, ratio of carrier weight to impregnation solution volume = 0.05 kg dm<sup>-3</sup>)

Cobalt compound	pH	Impregnation time, h	Equilibrium CoO concentration in catalyst, mass %
CoCl <sub>2</sub> · 6 H <sub>2</sub> O	5.7	2	1.12
Co(NO <sub>3</sub> ) <sub>2</sub> · 6 H <sub>2</sub> O	5.7	4	1.50
Co(HCOO) <sub>2</sub> · 2 H <sub>2</sub> O	6.3	6	2.25
[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>2</sub>	11.5	6	5.54

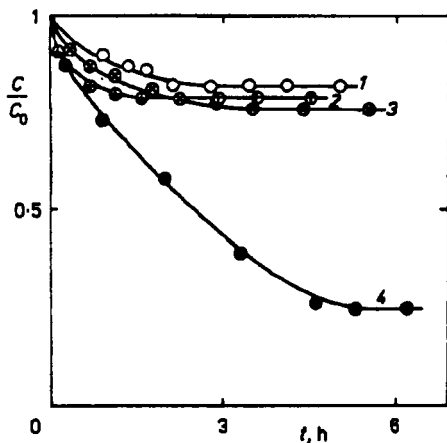


FIG. 1  
Kinetics of impregnation of  $\gamma$ -alumina B with cobalt compounds in aqueous medium. 1 Cobalt(II) chloride, 2 cobalt(II) nitrate, 3 cobalt(II) formate, 4 hexaamminecobalt(II) chloride

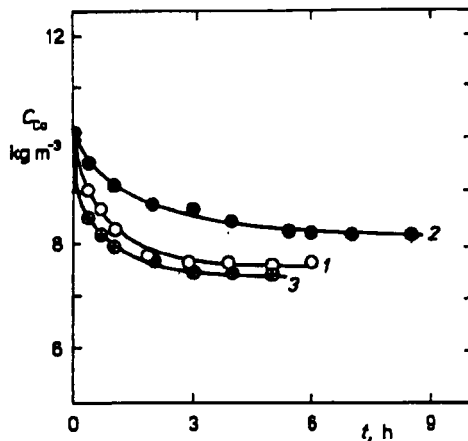


FIG. 2  
Kinetics of impregnation of cobalt [Co(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O] during competitive saturation of  $\gamma$ -alumina in aqueous medium. 1  $\gamma$ -Alumina A, 2  $\gamma$ -alumina B, 3  $\gamma$ -alumina C

components in the catalyst was reached in case of the chloride  $\gamma$ -alumina type C whereas the aluminate type B of  $\gamma$ -alumina showed the lowest adsorption ability (see Table II). The results obtained correlate well with the porosity of the carriers adopted which was measured with a Micromeritics autopore 9200 apparatus (Table II).

The catalyst activity can also be modified by changing the order of impregnations of the two components of hydrodesulfurization catalyst. Table III gives the composition and activities of the catalysts prepared by stepwise impregnations of  $\gamma$ -alumina A with

TABLE II

Effect of nature of  $\gamma$ -alumina on equilibrium concentration of cobalt and molybdenum oxides in catalyst after simultaneous impregnation ( $T = 293$  K, initial concentrations in solution:  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$   $C_0 = 50.18 \text{ kg m}^{-3}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$   $C_0 = 37.17 \text{ kg m}^{-3}$ ,  $t = 8.5$  h, ratio of carrier weight to impregnation solution volume =  $0.087 \text{ kg m}^{-3}$ )

Carrier	Type of $\gamma$ -alumina	Porosity %	Specific surface $\text{m}^2 \text{g}^{-1}$	Equilibrium concentration mass %	
				CoO	MoO <sub>3</sub>
A	alkoxide	54.3	207	3.00	13.10
B	aluminate	43.0	252	2.37	6.85
C	chloride	68.6	217	3.24	13.85

TABLE III

Effect of order of impregnations of cobalt and molybdenum compounds on catalyst activity ( $\gamma$ -alumina A,  $t = 6.5$  h,  $T = 298$  K, initial concentrations in solution:  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$   $C_0 = 50.18 \text{ kg m}^{-3}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$   $C_0 = 37.17 \text{ kg m}^{-3}$ , ratio of carrier weight to impregnation solution volume =  $0.087 \text{ kg dm}^{-3}$ )

Catalyst	Order of impregnations		Composition of catalyst, mass %		$k \cdot 10^5$ <sup>a</sup>
	1	2	CoO	MoO <sub>3</sub>	
MC	Mo	Co	0.6	8.6	1.63
CM	Co	Mo	1.0	8.3	1.87
Z	Co, Mo	-	3.0	13.1	2.35

<sup>a</sup> The rate constant in  $\text{dm}^3 \text{min}^{-1} \text{kg}_{\text{cat}}^{-1} \text{kPa}^{-1}$ .

molybdenum followed by cobalt salt (denoted as MC), cobalt followed by molybdenum salt (CM), or by competitive impregnation with both the components at the same time (Z). From Table III it clearly follows that the simultaneous impregnation with cobalt and molybdenum salts results in higher concentrations of the two components in the catalyst: this synergism can be caused by precipitation of  $\text{CoMoO}_4$  from dilute solutions affected by the alumina adopted. This fact, of course, also leads to a higher activity of the catalyst thus prepared, which is documented by the values of hydrodesulfurization rate constants.

### Hydrodesulfurization Activity of Catalysts

An example of measurement of conversion–time dependence in the hydrodesulfurization of gas oil is presented in Fig. 4 for selected samples of the synthesized and commercial catalysts. The reaction is first order with respect to the sulfur content in the reaction mixture<sup>10</sup>. The linear regression of these data according to the rate equation of the 1st order gave the hydrodesulfurization rate constants which, in the present communication, are considered to be a measure of catalyst activity. The rate constant values are summarized in Table IV. It is seen that, although the catalysts have (except the catalyst No. 2) roughly the same composition, their activity depends on both the carrier adopted and the procedure of preparation (the size and shape of catalyst

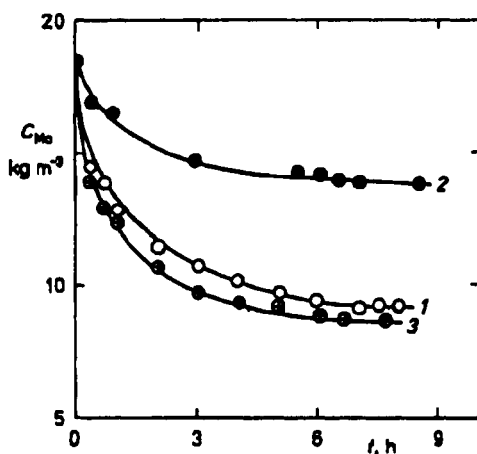


FIG. 3  
Kinetics of impregnation of molybdenum  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}]$  during competitive saturation of  $\gamma$ -alumina in aqueous medium. 1  $\gamma$ -Alumina A, 2  $\gamma$ -alumina B, 3  $\gamma$ -alumina C

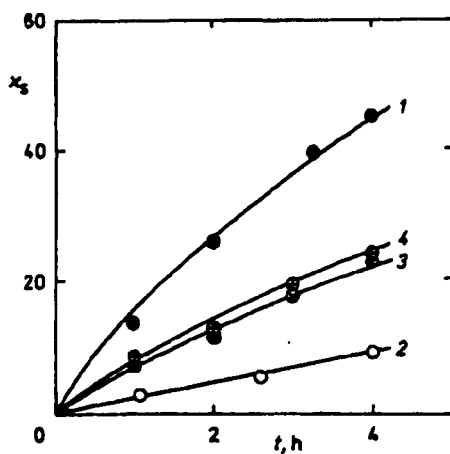


FIG. 4  
Conversion–time dependence of hydrodesulfurization of gas oil ( $T = 573 \text{ K}$ ,  $P = 3 \text{ MPa}$ ,  $m_k = 5 \text{ g}$ ). 1 Shell 344, 2 Cherox 36-01, 3 catalyst No. 1, 4 catalyst No. 3

particles, the provenience). Nevertheless, it can be stated that the catalyst No. 3 prepared by us shows a comparable activity with the catalysts of SHELL and AKZO. The properties of this catalyst were also measured in a wider temperature interval (543 – 623 K). Figure 5 adopting the Arrhenius coordinates shows the conversion–temperature dependence of hydrodesulfurization and hydrogenation of aromatic compounds in gas oil. The contents of aromatic compounds in the reaction mixture was evaluated by the aniline point<sup>16</sup>. The slopes of the two straight lines were used to calculate the activation energy values of hydrodesulfurization (75 kJ mol<sup>-1</sup>) and hydrogenation of aromatic compounds (32 kJ mol<sup>-1</sup>).

TABLE IV

Comparison of hydrodesulfurization activity of synthesized and commercial catalysts (reaction conditions:  $T = 573$  K,  $P = 3$  MPa,  $m_{\text{cat}} = 5$  g)

Catalyst	$\gamma$ -Alumina	Composition of catalyst, mass %		$k \cdot 10^5$ <sup>a</sup>
		CoO	MoO <sub>3</sub>	
1	A extr.	3.0	13.1	2.35
2	B extr.	2.37	6.85	1.94
3	C extr.	3.24	13.85	2.57
CHEROX 36-01	B pellets 4 × 6	4.1	12.6	1.6
SHELL 344	extr.	3.0	13.76	3.01
AKZO KF 702	extr.	3.62	12.89	2.38

<sup>a</sup> The rate constant in  $\text{dm}^3 \text{min}^{-1} \text{kg}_{\text{cat}}^{-1} \text{kPa}^{-1}$ .

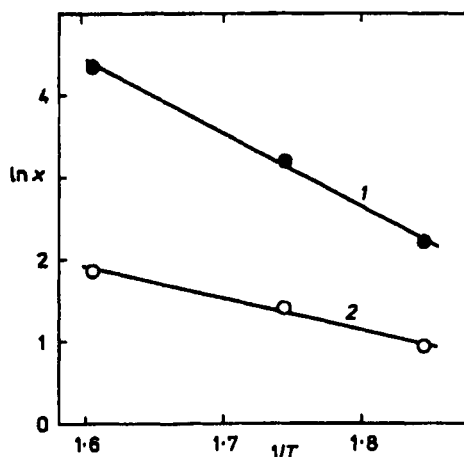


FIG. 5  
Conversion–temperature dependence of hydrodesulfurization and hydrogenation of aromatic compounds in gas oil. 1 Hydrodesulfurization, 2 hydrogenation of aromatic compounds

## SYMBOLS

$A$	rate of volume decrease of reaction mixture, $\text{ml h}^{-1}$
$C_{\text{Co}}$	concentration of cobalt, $\text{kg m}^{-3}$
$C_{\text{Mo}}$	concentration of molybdenum, $\text{kg m}^{-3}$
$k$	hydrodesulfurization rate constant, $\text{dm}^3 \text{min}^{-1} \text{kg}_{\text{cat}}^{-1} \text{kPa}^{-1}$
$m_{\text{k}}$	catalyst weight, g
$P$	partial pressure of hydrogen, MPa
$T$	absolute temperature, K
$t$	time, h
$x_{\text{S}}$	conversion of hydrodesulfurization, %

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