

COMPARISON OF MgO-SUPPORTED Ni-Mo HYDRODESULFURIZATION CATALYSTS PREPARED BY IMPREGNATION AND BY PRECIPITATION-ADSORPTION IN EMULSION

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Magnesia-supported Ni-Mo sulfide catalysts were prepared by several versions of aqueous impregnation method and by the unconventional method of precipitation-adsorption of sulfides in emulsion water-toluene. The activity of catalysts was tested in hydrodesulfurization of thiophene at pressure of 1.6 MPa. The samples of Ni-Mo/MgO prepared by impregnation exhibited only 15–30% of the activity of Ni-Mo/Al₂O₃ catalyst Shell 324; the principle obstacle was found to be chemical and hydrothermal instability of MgO with high surface area. The activity of samples prepared by precipitation-adsorption was not much lower than that of the impregnated catalysts; this was taken as an indirect evidence of the acid-base interaction between sulfides and MgO surface. It was concluded that the course of low activity of Ni-Mo/MgO catalysts was textural and not chemical; surface area of Ni-Mo active phase in MgO-supported catalysts was supposed to be lower than in Al₂O₃-supported catalysts.

Industrial Ni-Mo and Co-Mo sulfide hydrotreating catalysts are supported on alumina. However, interest in alternative supports such as carbon^{1,2}, silica³, titania⁴⁻⁷, zeolites^{8,9}, zirconia⁵ or magnesia^{5,7} is increasing recently.

Our interest in magnesia-supported sulfide catalysts is connected with basic character of magnesia. We expect that this character should strongly influence the selectivity of sulfide catalysts to various hydrorefining reactions as compared with the catalysts supported on more acidic alumina. This assumption is supported by literature: in comparison with alumina-supported catalysts, magnesia-supported catalysts were claimed to be more selective for hydrodesulfurization with minimum hydrogenation of olefins¹⁰, to have lower propensity to coking and metallation¹¹ and to have very small hydrocracking activity⁷.

However, the disadvantage of magnesia-supported sulfides is low activity; they are generally held for much less active than their alumina-supported counterparts⁵⁻⁷. In the literature, this fact seems to be attributed to the undesirable specific interaction of the active phase with magnesia. On the other hand, we believe that this low activity might be caused by improper preparation procedure, because only little work has been devoted to optimization of the preparation of magnesia-sup-

ported sulfides. The conventional preparation procedures known for alumina-supported catalysts were used for magnesia-supported catalysts in the literature, but these procedures are not necessarily optimum, because chemical character of alumina and magnesia is quite different.

The purpose of the present work was to get more experience with the preparation of Ni-Mo/MgO sulfide catalyst. Several different versions of aqueous impregnation method were evaluated. The attempt to prepare the catalyst by unconventional method of the precipitation-adsorption of sulfides in emulsion water-toluene was made.

The activity of catalysts was tested in hydrodesulfurization of thiophene at pressure of hydrogen of 1.6 MPa and was compared with the activity of commercial Ni-Mo and Co-Mo alumina-supported catalysts.

EXPERIMENTAL

Commercial alumina-supported catalysts. Two catalysts were used: (i) Ni-Mo/Al₂O₃, Shell 324, 17.7% MoO₃ and 3.4% NiO; (ii) Co-Mo/Al₂O₃, Cherox 3601 (Chemical Works, Litvínov, Czechoslovakia), 14.3% MoO₃ and 3.6% CoO.

Magnesia support. Three forms of MgO were used, one with medium and two with high surface area. The surface area cannot be characterized by a single value, because it is strongly dependent on the temperature pretreatment before measurement; the data are given in Results. The commercial fine powder of MgO (Labora, Czechoslovakia, grade "light") was denoted as MgO(1). The high surface area MgO(2) was prepared from MgO(1) by hydration-calcination treatment¹². The carrier MgO(3) was prepared by pelleting and crushing of MgO(1) to the particle size fraction 0.16–0.32 mm followed by the calcination at 400°C in flow of air. The carriers MgO(2) and MgO(3) were immediately used after calcination.

Impregnated MgO-supported catalysts. The amount of metal salts used corresponded to the composition of 12% MoO₃ and 3% NiO. The catalysts are denoted by letter I and are summarized in Table I.

The sample I1 was obtained by sequential wet impregnation. Slurry of 2.7 g MgO(1) in the solution of 0.47 g (NH₄)₆Mo₇O₂₄·4 H₂O in 50 ml of water was dried in rotary vacuum evaporator at 100°C and the product was calcined for 2 h at 400°C in flow of nitrogen. The resulting powder was added to the solution of 0.29 g NiCl₂·6 H₂O in 50 ml of water and the slurry was dried and calcined as above. The catalyst was pelleted and crushed to the particle size 0.16 to 0.32 mm. The catalyst I2 was prepared in the same way using nickel nitrate instead of chloride.

The samples I3–I5 were prepared by incipient wetness impregnation of the carrier MgO(3). The impregnation solution for the sample I3 was obtained by mixing hot solutions (60°C) denoted as A and B; the solution A contained 2.6 g (NH₄)₆Mo₇O₂₄·4 H₂O in 15 ml of water and the solution B contained 1.86 g NiSO₄·7 H₂O in 5 ml of water. The light precipitate formed after mixing was dissolved by adding of 15 drops of concentrated H₂SO₄ and heating to 90°C. The volume of the solution was adjusted by water to 21 ml; pH of it was 2. The volume of 2.1 ml of this hot solution (60°C) was added to 1.5 g of MgO(3). The sample was dried in rotary evaporator and calcined for 2 h at 400°C in stream of air.

The impregnation solution for the sample I4 was prepared in a slightly different way. The solution B was acidified by one drop of H₂SO₄ and was mixed with the solution A at ambient temperature. The resulting solution was stable for about 5 min.

The solution of MgMoO_4 for the preparation of sample I5 was obtained by heating of 2.12 g MoO_3 and 1.6 g MgCO_3 in 17 ml of water. The solution of 1.86 g $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ in 5 ml of water was added. The formed precipitate was dissolved by acidifying the solution by H_2SO_4 to pH 3 and by heating to 90°C. The volume was adjusted by evaporation to 21 ml and 2.1 ml of the solution was added to 1.5 g $\text{MgO}(3)$. The catalyst was dried and calcined as above.

Precipitated MgO-supported catalysts. The amount of metal salts corresponded to the same composition as for impregnated samples. The catalysts are denoted by the letter P.

In the preparation of sample P1, the solution of 0.47 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ and of 0.31 g of nickel acetate in 30 ml of water was mixed with the solution of 0.8 g surfactant Brij 35 (polyethyleneglycol–dodecylether, Fluka) in 150 ml of toluene. White emulsion was created by intensive stirring by vibrational agitator for 10 min. The mixture was left standing for 20 min without stirring and partial separation of the emulsion occurred. The mixture was stirred additional 5 min and the thick, stable emulsion resulted. The sulfides were precipitated by simultaneous addition of two solutions: 11.5 mmol $(\text{NH}_4)_2\text{S}$ in 4 ml of water and 11 mmol of H_2SO_4 in 4 ml of water. Each solution was fed by the rate of 2 ml min^{-1} , and the precipitation vessel was stirred manually. The mixture was standing for 1 h with occasional stirring. It was added 2.7 g $\text{MgO}(1)$ powder under stirring with vibrational stirrer. The mixture was filtered and the resulting paste was calcined in flow of nitrogen; the temperature was increased to 400°C during 1 h and was kept constant at 400°C for additional 0.5 h. The resulting, homogeneously dark brown powder was homogenized, pelleted and crushed to the particle size 0.16–0.32 mm.

The samples P2–P5 were prepared by slightly modified versions of this procedure. The deviation from the above basic procedure was for individual samples as follows:

P2: the carrier was added into the emulsion before precipitation;

P3: nickel chloride and HCl were used instead of nickel acetate and H_2SO_4 , respectively;

P4: chemicals used were as for P3; the mixture after precipitation was filtered, the wet solid was stirred for 0.5 h in 150 ml of toluene and carrier was added into the resulting slurry;

P5: $\text{MgO}(2)$ was used instead of $\text{MgO}(1)$.

TABLE I
Characterization and activity of catalysts prepared by impregnation and activity of commercial samples

Sample	Impregnation	Carrier	Method of impregnation	RA
I1	NiCl_2 , AHM ^a	$\text{MgO}(1)$	sequential wet	1.5
I2	$\text{Ni}(\text{NO}_3)_2$, AHM	$\text{MgO}(1)$	sequential wet	1.1
I3	NiSO_4 , AHM	$\text{MgO}(3)$	simultaneous incipient wetness	1.8
I4	NiSO_4 , AHM	$\text{MgO}(3)$	simultaneous incipient wetness	2.7
I5	NiSO_4 , MgMoO_4	$\text{MgO}(3)$	simultaneous incipient wetness	1.4
Shell 324	—	—	—	9.0
Cherox 3601	—	—	—	1.0

^a Ammonium heptamolybdate.

Catalytic test. Activity was determined using hydrodesulfurization of thiophene (TH) at the total pressure of 1.6 MPa in a tubular flow reactor with a fixed bed of catalyst. The catalyst charge was 0.01 g, the feed was hydrogen containing 400 molar ppm of TH; the flow of hydrogen was 0.8 mol h^{-1} .

The catalyst was in situ sulfided by the $\text{H}_2\text{S}/\text{H}_2$ mixture (1 : 10) under atmospheric pressure for 2 h. The feed was introduced at the pressure of 1.6 MPa and the conversion of thiophene, $x(\text{TH})$, was sequentially determined at several temperatures from 400 to 200°C, changing the temperature in steps of 20°C. It was checked by separate experiments that no deactivation of catalyst occurred for 8 h.

Surface area. BET surface area was measured by adsorption of nitrogen. Most of the data were obtained by single point flow method by Nelsen and Eggertsen¹³. The heat pretreatment of samples was various and is mentioned in the further text. The standard static BET measurement on Digisorb 2600 apparatus (Micromeritics) was also performed for some samples. The samples were heated at 400°C for 12 h in vacuum in this case.

RESULTS AND DISCUSSION

The purpose of the present work was to explore a broader range of preparation conditions rather than to study details of one preparation procedure. For this reason, the reproducibility of the preparation has mostly not been studied.

Chemistry of impregnation. The impregnation of alumina with ammonium heptamolybdate has been studied in detail in literature (e.g. refs¹⁴⁻¹⁷). However, magnesia differs from alumina in two respects: it is basic and it is hydrothermally unstable. The consequence of it for the impregnation process has not been discussed in the literature on sulfide catalysts.

During pore-filling or wet (excess of solution) impregnations of alumina with ammonium heptamolybdate, pH of the solution tends to rise toward the isoelectric point, ISP, of alumina^{14,16}. Luthra and Cheng¹⁶ used alumina with $\text{ISP} = 8.5$ and the pore filling method; the initial pH of the solution was 5.5 and the final pH was 6.5.

On the other hand, in all impregnations of MgO described in the present work (samples I1–I4), the final pH of the solution in pores was about 12, in spite of the very low initial pH of some solutions (initial pH = 2 for sample I3). (The final pH was measured by sucking off the solution from wet particles by indicator paper). Additional differences between alumina and magnesia were also observed: (i) the heat effect during the contact of MgO with impregnation solutions was higher than is usual for Al_2O_3 , (ii) ammonia is mostly retained in the sample during drying of alumina-supported catalysts and is removed only during calcination; in the case of magnesia-supported catalysts, ammonia volatilized from the sample already during drying, which is caused by the high final pH of the solution in pores, (iii) the surface area of dried Al_2O_3 -supported catalysts before calcination is only by about

10–20% lower than that of the support before impregnation; on the other hand, the area of dried MgO-supported samples was only about 10–30 m² g⁻¹, even when high surface area MgO(2) was used; this will be discussed more in detail henceforward.

Surface area. The hydrothermal instability of magnesia support is known in literature^{12,18,19}. High surface area MgO is converted to low surface area Mg(OH)₂ in aqueous environment or even upon storing at ambient atmosphere. The reverse chemical and textural changes occur during calcination. In the measurement of surface area, the result depends strongly on the temperature pretreatment of the sample. Our results in this respect agree with the literature. The area of MgO(1) was 70 m² g⁻¹. It increased to 90 and 160 m² g⁻¹ after heating it in flow of air or nitrogen for 15 min at 220°C and for 2 h at 400°C, respectively. The sample MgO(3) behaved in the same way. The area of dried Mg(OH)₂, which was the intermediate in the preparation of MgO(2), was 30 m² g⁻¹. The area of MgO(2) was 250 m² g⁻¹. The high surface area of carriers MgO(2) and MgO(3) was not stable in ambient atmosphere.

The hydrothermal instability of MgO complicates the preparation of MgO-supported metal catalysts by impregnation in water solutions. Because of chemical and textural changes occurring during impregnation and drying, a part of metal might be trapped inside the solid¹⁹. However, these aspects have not been considered in the literature on sulfide catalysts.

The behaviour of all Ni–Mo/MgO catalysts prepared here was qualitatively similar to the behaviour of the MgO alone. For example, the area of the sample I2 preheated to the temperature 250°C was 30 m² g⁻¹ (the area of starting MgO(1) was 70 m² g⁻¹) and increased to 100 and 130 m² g⁻¹ after heating to 340 and 400°C, respectively. The standing of the sample for 2 days caused the decrease of surface area to 60 m² g⁻¹. Similarly, the surface area of dried sample I3 was 10 m² g⁻¹ (the area of starting MgO(3) was 160 m² g⁻¹) and it increased to 300 m² g⁻¹ after calcination at 400°C.

The surface areas obtained with Digisorb apparatus after pretreatment at 400°C in vacuum were by 50–100% higher than the areas obtained by single point flow method after pretreatment at 400°C for 15 min in air. This our observation concerning Ni–Mo/MgO catalysts is similar to the results by Wanke and Fiedorov¹⁹ concerning MgO alone.

In summary, the surface area of Ni–Mo/MgO catalysts in oxidic form was changeable and responded to temperature and to moisture in the same way as the carrier system MgO–Mg(OH)₂ alone. It is concluded that the high surface area developed during calcination of our catalysts was formed by MgO surface, not covered by the active oxides. The surface area of active phase was probably rather low, only about 10–30 m² per gram of catalyst. This conclusion is also supported by activity data discussed henceforward.

Evaluation of activity. The typical dependences of the conversion $x(\text{TH})$ on temperature are shown in Fig. 1. Our previous experience with various catalysts showed that under conditions of our test (fixed pressure and initial concentration of reactants), the dependence $x(\text{TH})$ on catalyst charge W in the range of $x(\text{TH})$ from 0.01 to 0.90 can be described by pseudo-first order kinetics with the rate constant k . Space time was the same for all catalysts and Eq. (1) can be written for each temperature

$$\frac{\ln(1 - x(\text{TH}, i))}{\ln(1 - x(\text{TH}, s))} = \frac{k(i)}{k(s)}, \quad (1)$$

where i and s denote i -th and standard catalysts, respectively. The Co-Mo/Al₂O₃ catalyst Cherox 3601 was chosen as the standard catalyst. The dependence obtained by plotting the conversions from Fig. 1 in coordinates of Eq. (1) were approximately linear for all catalysts. The slope of these lines has the meaning of the relative rate constant $k(i)/k(s)$ and is denoted as relative activity of catalyst i , $\text{RA}(i)$. It characterizes the behaviour of catalyst i in the whole region of temperatures used.

The reproducibility of the activity testing, including reproducibility of sulfidation was better than $\pm 10\%$ of the value of $\text{RA}(i)$.

Activity of commercial catalysts. Table I shows that the difference in RA of both commercial catalysts was almost one order of magnitude. Catalyst Cherox 3601 is an old-generation catalyst produced by coprecipitation of alumina with oxides of active metals. The catalyst Shell 324 is a relatively modern catalyst produced presumably by impregnation.

Activity of impregnated catalysts. The activities RA are summarized in Table I.

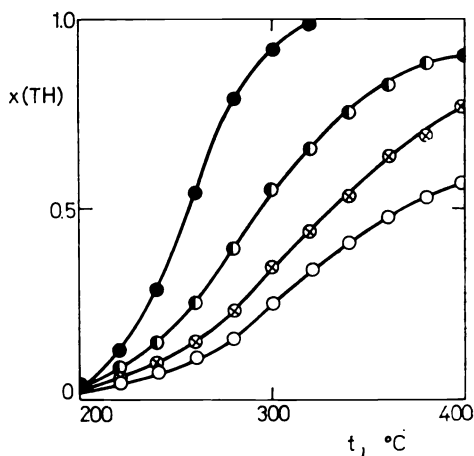


FIG. 1

Temperature dependence of thiophene conversion ● Shell 324, ● I4, ⊗ P1, ○ Cherox 3601

They varied in the range 1.1–2.7, and were thus intermediate between the activity of both commercial catalysts.

It was suggested that chlorides should be avoided in the preparation of MgO-supported metal catalysts, because Cl ions exhibit detrimental effect on surface area of MgO; however, this was not documented by activity data^{18,19}. Our results on samples I1 and I2 in Table I showed no negative effect of chlorine on the activity. The effect of chlorine was probably superimposed by the effect of other factors deteriorating the texture of MgO, i.e. the presence of other ions and the drying at high temperature.

The samples I3 and I4 prepared by simultaneous impregnation were more active than I1 and I2 prepared by sequential impregnation. This is explained by longer contact of carrier with solutions during sequential impregnation, which leads to deeper texture changes as compared with the simultaneous impregnation.

The comparison of samples I3 and I4 in Table I suggests that too low pH of the impregnation solution is unfavourable for the activity (pH was 2 and 6, respectively). This indicates the principal difficulty in the preparation of Ni–Mo catalysts by incipient wetness simultaneous impregnation. The stable concentrated solutions containing both metals are acidic (pH of the often used solutions stabilized by H₃PO₄ is in the range 2–4, refs^{20–22}) and undoubtedly would solubilize part of MgO support. On the other hand, neutral solutions which do not attack MgO carrier are unstable.

The use of MgMoO₄ instead of (NH₄)₆Mo₇O₂₄ in the preparation of the sample I5 was an attempt to exclude ammonia from the procedure. However, the activity of catalyst was relatively low. We believe that this is caused more by the low pH of the impregnation solution than by the use of MgMoO₄.

Activity of precipitated catalysts. In designing the unconventional precipitation–adsorption method, we combined the experience of other authors in two different areas: (i) sulfides dispersed colloiddally in non-aqueous solvent were easily adsorbed on MgO which was explained by acid–base interaction²³, (ii) emulsion served as discontinuous reaction medium in the preparation of NiB hydrogenation catalyst; fine and uniform particles were obtained²⁴.

We assumed that precipitation in emulsion will provide fine dispersion of sulfides which will be stabilized by specific adsorption on MgO even in the presence of water. These assumptions were confirmed by relatively high activity of the sample P1 shown in Table II, which was comparable to the activity of impregnated catalysts. The catalysts precipitated in water instead in emulsion, the unsupported samples precipitated in emulsion and the samples precipitated in emulsion and supported on γ -alumina, kieselguhr, α -alumina or silica were almost inactive having RA in the range 0.01–0.15. The specific interaction between sulfides and MgO was also confirmed visually. White particles of MgO were covered by dark particles of sulfides

and the colour of the mixture was homogeneous. On the other hand, the colour of the catalysts with alumina or kieselguhr was inhomogeneous with white conglomerates of carrier particles.

The preparation of the sample P1 was repeated three times and the activities RA obtained were 1.6, 1.4, and 1.6, which proved the reasonable reproducibility of the method.

In an attempt to improve the activity of the sample P1, the samples P2–P5 were prepared by the modified procedures described in Experimental and in Table II. However, the effect of all modifications tried was small. In agreement with our experience with impregnated catalysts, no negative effect of Cl ions on the activity was observed.

In the precipitation–adsorption method, the surface in narrow pores of the carrier was certainly not accessible to deposition of sulfide particles. In spite of this, the activity of precipitated catalysts was similar to the activity of impregnated catalysts. This supports the conclusion made above from surface area measurements: fine texture of high surface area MgO is damaged during aqueous impregnation and the surface area of active phase is rather low in impregnated catalysts.

CONCLUSIONS

The chemical and hydrothermal instability of high surface area MgO is a principle obstacle in the preparation of Ni-Mo/MgO catalysts by aqueous impregnation. Because of changes in the texture of the support during impregnation, drying and calcination, the area of active phase is lower than in an alumina-supported catalysts. The repeated contact of carrier with aqueous solutions and the use of acidic solutions solubilizing MgO should be avoided. One-step simultaneous wetness impregna-

TABLE II
Activity of catalysts prepared by precipitation–adsorption

Catalyst	Characteristic feature of preparation ^a	RA
P1	standard precipitation	1.5
P2	carrier added before precipitation	1.4
P3	chlorides present	1.6
P4	chlorides present, carrier added in toluene	1.2
P5	carrier MgO(2)	1.2

^a Full details are presented in text.

tion with neutral solution led to the best activity among alternative impregnation procedures.

The particles of sulfides, which possess surface Lewis acidity, specifically interact with MgO. The mixing of fine dispersions of sulfides, obtained by precipitation in emulsion water-toluene, with MgO powder led to catalysts exhibiting the activity comparable to catalysts obtained by impregnation.

The activity of catalysts prepared was on the level of 15–30% of the activity of commercial Shell Ni–Mo/Al₂O₃ catalyst. The cause of the low activity is textural and not chemical; surface area of Ni–Mo active phase in MgO-supported catalysts is lower than in Al₂O₃-supported catalysts. The collapse of texture of high surface area MgO during preparation of Ni–Mo/MgO catalyst in water solutions cannot be hindered. This situation invites the research on the preparation of Ni–Mo/MgO catalysts by non-aqueous impregnation.

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