Preparation of alumina supported molybdena catalysts by new slurry impregnation method: MoO_3/Al_2O_3 sulfide hydrodesulfurization catalyst

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A new slurry impregnation method (SIM) of the preparation of a catalyst or catalyst precursor MoO_3/Al_2O_3 is described. Aqueous slurry of powdered MoO_3 is mixed with alumina extrudates and the mixture is refluxed. A low solubility of MoO_3 is sufficient for transport of MoO_3 from powder form via solution to the surface of the support. The catalysts were tested by hydrodesulfurization of thiophene at 1.6 MPa and 280–400°C. Their activity was similar to the activity of industrial and laboratory MoO_3/Al_2O_3 samples prepared by conventional impregnation with solution of ammonium heptamolybdate. The advantage of the SIM method is that calcination, producing nitrogeneous waste gases, is not required and that all deposited molybdenum species are adsorbed and not precipitated.

Keywords: alumina supported molybdena catalysts; unconventional impregnation method; hydrodesulfurization

1. Introduction

Alumina supported molybdenum based catalysts in oxidic, reduced, or sulfided forms are active in a great number of reactions. The common precursor of catalysts in various forms is molybdenum(VI) oxide supported on alumina, MoO_3/Al_2O_3. It is industrially manufactured by impregnation of an alumina support with a solution of ammonium heptamolybdate and consecutive calcination [1,2]; the older alternative technology was the coprecipitation of MoO_3 and Al_2O_3. Impregnation with ammonium heptamolybdate also remains the most important technique used on a laboratory scale even when a number of alternative procedures using various other molybdenum compounds have been reported in the literature. Chemistry, physical chemistry and chemical engineering of the conventional impregnation with ammonium heptamolybdate have been extensively studied (see for instance refs. [2–9]).

Ammonium heptamolybdate used in the classical impregnation is a very soluble compound with the solubility of about 50 and 140 g of MoO_3 per 100 ml of water at 25 and 65°C, respectively [10]. On the other hand, the new impregnation method described in the present work uses the very sparingly soluble MoO_3, the solubility of which is about 0.1 and 2.1 g per 100 ml of water at 18 and 70°C, respectively [11]. The required amount of MoO_3 is mixed with the support in a small volume of water. Molybdenum species are transformed from the solid MoO_3 to the surface of the support by dissolution and adsorption, until all solid MoO_3 disappears. This new technique may be called slurry impregnation method, with the acronym SIM, because the molybdenum compound is added to the support in the form of a slurry and not a solution.

Several catalysts MoO_3/Al_2O_3 were prepared by the SIM technique in the present work. After presulfidation, the samples were tested by hydrodesulfurization of thiophene. The activity was compared with the industrial and laboratory-made MoO_3/Al_2O_3 catalysts prepared by conventional impregnation with ammonium heptamolybdate.

2. Experimental

2.1. SUPPORTS

γ-alumina Norton 6173 (Norton Chemical Process Products, UK) is named here Al(N); the diameter of the extrudates was 1.6 mm, BET surface area and pore volume were 195 $m^2\ g^{-1}$ and 0.62 $cm^3\ g^{-1}$, respectively. γ-alumina Spheralite SCS 250 (Rhone-Progil, France) is named here Al(S); the diameter of the spheres was 3–4 mm and the texture data were 305 $m^2\ g^{-1}$ and 0.53 $cm^3\ g^{-1}$, respectively.

The supports were impregnated either in the form of the original particles or they were crushed to particles of the size 0.16–0.32 mm.

2.2. CATALYSTS

The acronyms SIM and CIM represent the slurry impregnation method using a slurry of MoO_3 in water and the classical impregnation method using a solution of ammonium heptamolybdate, respectively. The catalysts were named according to the example: SIM-15MoO_3/Al(N), which is the catalyst containing 15% of MoO_3 and 85% of the alumina Norton, and prepared by the slurry impregnation method.

Molybdenum oxide MoO_3 (Fluka, p.a.) was used either as obtained or it was ground 0.5 h in an agate mortar before use.

The catalysts were dried in a rotary vacuum evaporator (90–100°C, 4–6 kPa) for 0.5 h. The CIM catalyst was calcined in a tubular flow reactor in a stream of air; the temperature was increased linearly during 1 h to 400°C and kept at this value for another 1 h. The SIM catalysts were not calcined.

In the SIM preparations, the slurry of the carrier and MoO_3 in water was refluxed. The intensity of boiling was kept minimal in order to avoid the attrition of the support particles. The turbid liquid remaining after separation of the impregnated particles of the support, was dried and the powder obtained was weighed. The purpose of this was to check that the amount of the unadsorbed molybdenum species was negligible. This powder was not analyzed but it was assumed that it was formed mostly by fine particles of the support mixed with a smaller amount of MoO_3.

The prepared and tested catalysts are summarized in table 1. The commercial catalyst 15% MoO_3/Al_2O_3, BASF M-8-30, was included as the reference point of activity.

SIM-20MoO_3/Al(S). The mixture of 6.8 g of the support in the form of original particles, 1.5 g of ground MoO_3 and 50 ml of water was refluxed for 6 h; most of the MoO_3 powder disappeared. After standing overnight at room temperature, the mixture was refluxed for 2 h; the remaining MoO_3 powder disappeared. The spheres of the impregnated support were separated from the slightly turbid liquid by pincette and were dried. The turbid liquid was dried and 0.3 g of powder was obtained.

SIM-17MoO_3/Al(N). The slurry of 3.4 g of the support extrudates, 0.62 g of ground MoO_3 and 25 ml of water was refluxed for 2 h; most of the MoO_3 powder disappeared. After standing overnight at room temperature, it was refluxed for another 2 h and the remaining MoO_3 powder disappeared. The extrudates were separated by pincette and dried. The turbid liquid was dried and 0.08 g of powder was obtained.

CIM-13MoO_3/Al(N). The solution of 1.41 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 10 ml of water was poured on to 10 g of the support, particle size fraction 0.16–0.32 mm. The mixture was left standing overnight at room temperature and dried and calcined as described above.

Table 1
The prepared MoO_3/Al_2O_3 catalysts and their relative hydrodesulfurization activity[a]

Catalyst j[b]	Impregnated particles	$k(j)/k(\mathrm{r})$
laboratory made catalysts		
SIM-20MoO_3/Al(S)	original spheres	1.0
SIM-17MoO_3/Al(N)	original extrudates	1.4
CIM-13MoO_3/Al(N)	fraction 0.16–0.32 mm	1.0
commercial catalyst		
15%MoO_3/Al_2O_3		
BASF M-8-30	–	1.0

[a] $k(j)/k(\mathrm{r})$ is relative activity defined by eq. (1), the reference catalyst is a commercial sample BASF M-8-30.

[b] SIM: slurry impregnation method; CIM: conventional impregnation method.

2.3. MEASUREMENT OF CATALYTIC ACTIVITY AND SURFACE AREA

All the catalysts were tested as particles of 0.16–0.32 mm (the catalysts prepared in the form of extrudates or spheres were crushed). The model reaction was hydrodesulfurization of thiophene. The integral conversion data were obtained in a fixed bed flow reactor. The total pressure was 1.6 MPa, the initial pressure of thiophene (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 presulfided in situ with a H_2S/H_2 mixture (1 : 10) at atmospheric pressure and 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 280°C, changing the temperature in steps of 20°C. The conversion was defined as $x(\mathrm{TH}) = [n^0(\mathrm{TH}) - n(\mathrm{TH})]/n^0(\mathrm{TH})$, where n^0 and n are the initial and final number of moles, respectively. The conversions were in the range 0.01–0.50, depending on the catalyst and temperature. The test lasted about 9 h, and no deactivation of the catalyst was observed.

BET surface area was measured by adsorption of nitrogen at −78°C using a Digisorb 2600 V4.02 (Micromeritics) instrument.

3. Results

3.1. SURFACE AREA

The support is heated in aqueous slurry for several hours in the SIM impregnation method and this might affect its texture. This possibility was checked by the measurement of surface area of the SIM catalysts and corresponding supports and the results are shown in table 2. It is seen that the difference in surface area caused by SIM impregnation is lower than 10%. When the surface area of the catalysts is normalized to 1 g of support in the catalyst, the increase of the surface of the support is observed for both aluminas. It is concluded that the SIM procedure has no important negative effect on the surface area of the support.

Table 2
The effect of slurry impregnation on the surface area of alumina support

Sample	BET surface area (m^2 g^{-1})	
	per g of sample	per g of support
Al(S)	305	305
SIM-20MoO_3/Al(S)	278	345
Al(N)	195	195
SIM-17MoO_3/Al(N)	209	251

3.2. CATALYTIC ACTIVITY

The catalysts were tested under fixed pressure of hydrogen, initial concentration of TH and feed rate F(TH), and the molar ratio hydrogen/TH was high. We have previously checked with other catalysts that under these limiting conditions, the dependence $x(\mathrm{TH}) = f(W/F(\mathrm{TH}))$ follows in the range of x(TH) from 0.01 to 0.90 the pseudo-first-order rate equation with the apparent rate constant k. All catalysts were tested at the same fixed space time W/F(TH) and at several temperatures. For each temperature the following equation can be written:

$$\ln[1 - x(\mathrm{TH},j)] = \frac{k(j)}{k(\mathrm{r})}\ln[1 - x(\mathrm{TH},\mathrm{r})], \qquad (1)$$

where j and r denote the jth and the reference catalyst, respectively. The commercial MoO_3/Al_2O_3 catalyst BASF M-8-30 was chosen as the reference catalyst in the present work. Straight lines were obtained by plotting conversions x(TH) at various temperatures according to eq. (1); this is illustrated in fig. 1. It is concluded that the apparent activation energies of samples tested are the same. The ratios $k(j)/k(\mathrm{r})$ obtained from the slopes of the lines in fig. 1 are the parameters independent of temperature. They characterize the relative activity of the catalysts in the whole range of temperatures measured, 280–400°C, and are shown in table 1.

The content of MoO_3 in the catalysts in table 1 was not constant and varied between 13 and 20% MoO_3. This makes the detailed comparison of activity rather

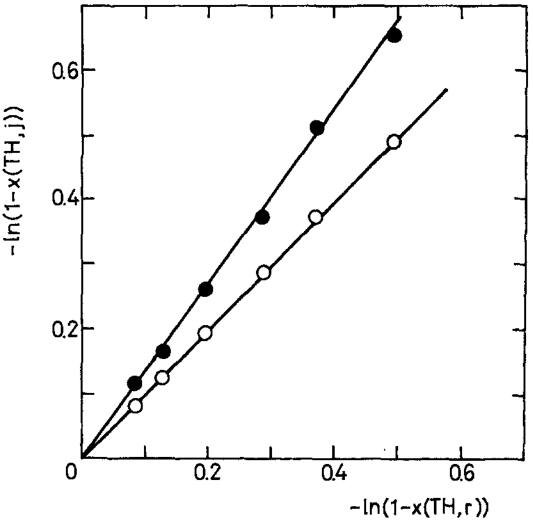

Fig. 1. Determination of the relative pseudo-first-order rate constants by plotting the conversions of hydrodesulfurization of thiophene at various temperatures of 280–400°C in the coordinates of eq. (1). jth catalysts: (●) SIM-17MoO_3/Al(N), (○) SIM-20MoO_3/Al(S); r: reference catalyst MoO_3/Al_2O_3 BASF M-8-30.

uncertain. However, the data in table 1 are quite sufficient to demonstrate that activity of SIM catalysts was at the same level as that of the conventional industrial and laboratory samples.

4. Discussion

Two types of molybdenum species are present in the dried uncalcined material after classical impregnation with ammonium heptamolybdate: adsorbed molybdate anions and microcrystals of ammonium heptamolybdate precipitated in the pores in the course of drying. The adsorbed species are commonly considered to be more desirable than microcrystals because it is believed that the adsorbed species are the precursor of a highly dispersed oxidic, reduced or sulfidic active phase in the finished catalyst. The adsorbed species predominate in those samples prepared by the equilibrium adsorption method. The incipient wetness (pore filling) impregnation, or drying the mixture of the support with volumetric excess of the solution gives a larger amount of the precipitated phase.

The important advantage of the new slurry impregnation method is that in the end the impregnation solution contains only a very small amount of the dissolved molybdenum species. The precipitation in the pores in the course of drying is negligible and practically all the deposited species are adsorbed species.

The driving force of the adsorption of molybdenum species is the difference between the chemical potentials of molybdate anions in solution and anions adsorbed on the surface. The concentration of dissolved molybdate anions in the slurry MoO_3–water is very low but it does not necessarily mean that the potential of them is also low. Our present results indirectly indicate that this potential is high: high loadings of typical alumina of about 15–20% of MoO_3 were achieved.

As reported by previous authors [12–16], the experimentally observed loading at which filling of the monolayer of MoO_3 on alumina occurs, corresponds to an area of 0.17–0.25 nm^2 per molecule of MoO_3. (Area of one molecule of MoO_3 at the surface of solid MoO_3 calculated by the method of Emmett and Teller is 0.154 nm^2 [17].) Using the value of 0.25 nm^2 per molecule of MoO_3, the monolayer loadings of our aluminas, Al(N) and Al(S), are 16 and 23% MoO_3, respectively. The successful preparation of the catalysts SIM-17MoO_3/Al(N) and SIM-20MoO_3/Al(S) proved that high loadings, close to monolayer loading, can be achieved by the SIM method.

The SIM method is very clean in the sense that no additional chemicals beside MoO_3 and water are introduced to the support during impregnation. In this respect, thermal spreading of MoO_3 [2,18–20] and vapour phase deposition of $Mo_2(OH)_2$ (e.g. ref. [13]) are similar methods. However, both latter methods use high temperatures of 450–600°C and thermal spreading also requires intimate mixing of fine powders of MoO_3 and Al_2O_3. On the other hand, the temperature used in SIM method is low and uncrushed extrudates or pellets of alumina support can easily be impregnated.

A certain disadvantage of the slurry impregnation method is kinetical. Because of the low concentration gradient, the rate of transport of MoO_3 from solid to adsorbed phase is low. The preliminary results of the present work have shown that several days, or even weeks, are necessary to accomplish the impregnation at room temperature (the time required depends on the amount of MoO_3 to be deposited). It was found that the process can be accelerated by an increase in temperature; boiling also ensures proper mixing and that impregnation is finished in several hours. It is important that the increase in temperature did not decrease the adsorbed amount; the catalysts with usual loading of 13–20% MoO_3 were prepared.

In conclusion, the advantages of the new slurry impregnation method of preparation of MoO_3/Al_2O_3 catalyst can be summarized: calcination is not required and the evolution of nitrogeneous gases is avoided, no other compounds beside H_2O and MoO_3 are involved, all deposited molybdenum species are adsorbed, precipitation in pores during drying is negligible, waste solutions are not produced, and activity of SIM catalysts is comparable to activity of catalysts prepared by the conventional impregnation.

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