Preparation of MoO_3/Al_2O_3 catalysts with sharp eggshell Mo distribution by slurry impregnation

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MoO_3/Al_2O_3 catalysts with eggshell Mo concentration profiles were prepared by reaction of Al_2O_3 extrudates or balls with slurry of MoO_3 in water. The Mo concentration wave penetrating Al_2O_3 particles during this slurry impregnation was almost rectangular. Its height was close to the filled monolayer loading. The thickness of the shell was regulated either by impregnation time or by the MoO_3 amount in the slurry. The hydrodesulfurization activity of Mo species deposited by slurry impregnation was about the same or better (depending on the Al_2O_3 used) as in industrial MoO_3/Al_2O_3 catalyst.

KEY WORDS: MoO_3/Al_2O_3 catalyst; eggshell Mo catalyst; slurry impregnation; hydrodesulfurization

1. Introduction

Catalysts based on supported MoO_3 show many applications in reactions of industrial importance such as oxidation, hydrotreatment, hydrocracking, metathesis, and isomerization [1].

Preparation of MoO_3/Al_2O_3 catalysts with eggshell Mo concentration profile is of both fundamental and practical interest. Previous authors prepared such catalysts by conventional impregnation using $(NH_4)_6Mo_7O_{24}$ solution. Lower pH and higher concentration of the solution and higher temperature and faster drying promoted the formation of an eggshell profile [2–6]. However, the profiles obtained were diffuse and shallow. Profiles with high Mo concentration and a rectangular shape that remain sharp and deep with increasing shell thickness have not been obtained by that method. For instance, Fierro *et al.* [4] achieved the profile with a concentration of 15 and 9 wt% MoO_3 at the surface and in the centre of the Al_2O_3 pellets, respectively (the diameter of the pellets was 3.2 mm and the surface area was 120 $m^2\,g^{-1}$).

In the present work, Al_2O_3 extrudates and balls were impregnated by reaction with slurry MoO_3/water. Low solubility of MoO_3 is sufficient for transport of Mo species into the interior of support particles. The method is named "slurry impregnation", SIM. In the previous papers it was used for impregnation of small Al_2O_3 particles (0.16–0.32 mm) [7,8] or for impregnation of Al_2O_3 extrudates with uniform (saturated) Mo concentration across the extrudates [9]. The preparation of eggshell-type catalysts described in the present work is a new application of SIM.

The methods used in the literature for evaluation of Mo profiles in Al_2O_3 extrudates or tablets included electron probe micro-analysis, EPMA, and reduction with hydrazine-hydrochloric solution or with gaseous hydrogen [2–6]. Two methods, EPMA and sulfidation of catalysts, were used in the present work. Sulfidation has not been previously used for this purpose in the literature and it was found very useful in the present work.

In order to characterize the activity of the Mo species deposited by SIM, saturated catalysts with uniform Mo distribution were also prepared and tested in hydrodesulfurization, HDS, of thiophene. Activity was compared with a commercial MoO_3/Al_2O_3 catalyst.

2. Experimental

2.1. Alumina supports

Akzo HDS-000-1.5 alumina (Akzo Chemicals, The Netherlands) is intended as a support of hydrotreating catalysts. It contained 1.3 wt% of SO_4^{2-}. The diameter of extrudates was 1.6 mm. Its BET surface area, pore volume and BJH average pore diameter was 262 $m^2\,g^{-1}$, 0.60 $cm^3\,g^{-1}$ and 8.2 nm, respectively.

Alcoa S-l00 alumina (Alcoa Industrial Chemicals, USA) was developed for the Claus process. The diameter of the balls was 5 mm. Its BET surface area, pore volume and BJH average pore diameter was 279 $m^2\,g^{-1}$, 0.37 $cm^3\,g^{-1}$ and 5.0 nm, respectively.

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2.2. Catalyst preparation

MoO_3 (Fluka, +99.5%) was ground in an agate mortar before use and its particle size distribution was determined using a Laser Granulometer Analysette (Fritsch). The number of particles with diameter smaller than 0.3, 1.0, 5.0, 10.0 and 20.0 μm was 12, 38, 76, 93 and 99%, respectively.

Nominal loading ($MoO_3/(MoO_3+Al_2O_3)$) corresponds to the MoO_3 amount in the impregnation slurry used. The actual loading was determined by EPMA and AAS.

The nominal loadings up to 18 and 20 wt% MoO_3 were somewhat lower than the saturated adsorption loadings of the Akzo and Alcoa aluminas, respectively (see Results and Discussion) and all MoO_3 powder disappeared at the end of impregnation. The nominal loading of 30% was higher than the saturated adsorption loading of both aluminas and part of the MoO_3 remained in the slurry at the end of impregnation. Samples were separated from the impregnation slurry by decantation (independently of whether all MoO_3 was consumed or not at the given impregnation time) and were dried in a rotary vacuum evaporator at 100 °C for 1 h. The catalysts were not calcined.

Impregnation at 100 °C. Mixture of alumina extrudates or balls (10 g) with the impregnation slurry MoO_3/water was heated under a reflux condenser to 100 °C (vigorous boiling was avoided to minimize the attrition of support particles). The level of water was about 3 mm above the layer of support particles.

For nominal loadings of 15 and 30%, a sample of five extrudates or balls was taken out at time intervals during impregnation (see Results and Discussion). For other loadings, no samples were taken out in the course of impregnation and the impregnation was finished when all MoO_3 disappeared from the impregnation slurry. (The impregnation times were 1 and 8 h for Akzo loading of 5 and 19%, respectively, and 4 and 18 h for Alcoa loading of 8 and 21%, respectively).

Impregnation at 25 °C. The mixture of alumina extrudates (10 g) with the impregnation slurry MoO_3/water was left standing at room temperature with occasional shaking. Otherwise, the procedure was the same as described above for impregnation at 100 °C.

2.3. Evaluation of Mo profiles

Radial Mo profiles were evaluated by two methods: EPMA and sulfidation. The sensitivity of both methods was tested using the sample 1% MoO_3/Al_2O_3 prepared by conventional impregnation of Akzo alumina with a solution of $(NH_4)_6Mo_7O_{24}$.

A JEOL JXA electron microscope was equipped with the ED analyser EDAX PV 9400. Each point in the graphs shown below represents the average loading of a square with the centre of the square at the distance from the extrudate or ball centre plotted on the x-axis. The dimension of the square was $60 \times 60\,\mu$m and $200 \times 200\,\mu$m for extrudates and balls, respectively. However, the points close to the surface of particles were also inspected using a narrow beam of $1 \times 1\,\mu$m. Two extrudates or two balls of each sample were measured and the profiles obtained were practically identical.

Samples were sulfided in the flow of an H_2S/H_2 mixture at 400 °C for 2 h. Light grey MoO_3 was transformed to black MoS_2 and the colour of white Al_2O_3 was not changed. Extrudates and balls were halved and photographed by a conventional camera. The pictures were transformed into electronic form by scanning. However, the Mo loading cannot be measured by this method.

2.4. Hydrodesulfurization activity

Activity of saturated samples with uniform Mo distribution was tested using HDS of thiophene (TH) in a flow reactor at a pressure of 1 MPa. The catalyst (weight $W = 0.03$ g, particle size fraction of 0.16–0.32 mm) was *in situ* presulfided in the flow of an H_2S/H_2 mixture at 400 °C for 1 h. The conversion x_{TH} was determined at several temperatures from 400 to 250 °C. The flow rate of TH (F_{TH}) and H_2 (F_{H_2}) was 0.43 and 1100 mmol h^{-1}, respectively.

The reference point of activity was commercial 15 wt% MoO_3/Al_2O_3 catalyst BASF M 8–30 (210 $m^2\,g^{-1}$).

3. Results and discussion

3.1. Specific features of slurry impregnation

Slurry impregnation belongs to equilibrium adsorption impregnation methods. However, it possesses important specific features.

The natural pH of the slurry MoO_3/water (about 2.8) is well below the point of zero charge of typical Al_2O_3 supports (about 6–8). The adsorption of molybdate anions is strong under these conditions and this leads to deep and sharp Mo concentration profiles.

In conventional equilibrium adsorption impregnation using a solution of $(NH_4)_6Mo_7O_{24}$, the concentration and the chemical potential of dissolved Mo species decrease as the system moves to adsorption equilibrium. That decrease can be minimized, and adsorption can be performed at approximately constant solution concentration, by using a large excess of the impregnation solution. The disadvantage of this arrangement is that a large volume of waste Mo solution remains after impregnation.

In the slurry impregnation, the presence of solid MoO_3 in the slurry keeps the concentration and chemical potential of dissolved Mo species constant (the solution remains saturated from the beginning until the end of impregnation). For nominal loadings higher than filled monolayer loading the adsorption proceeds until the

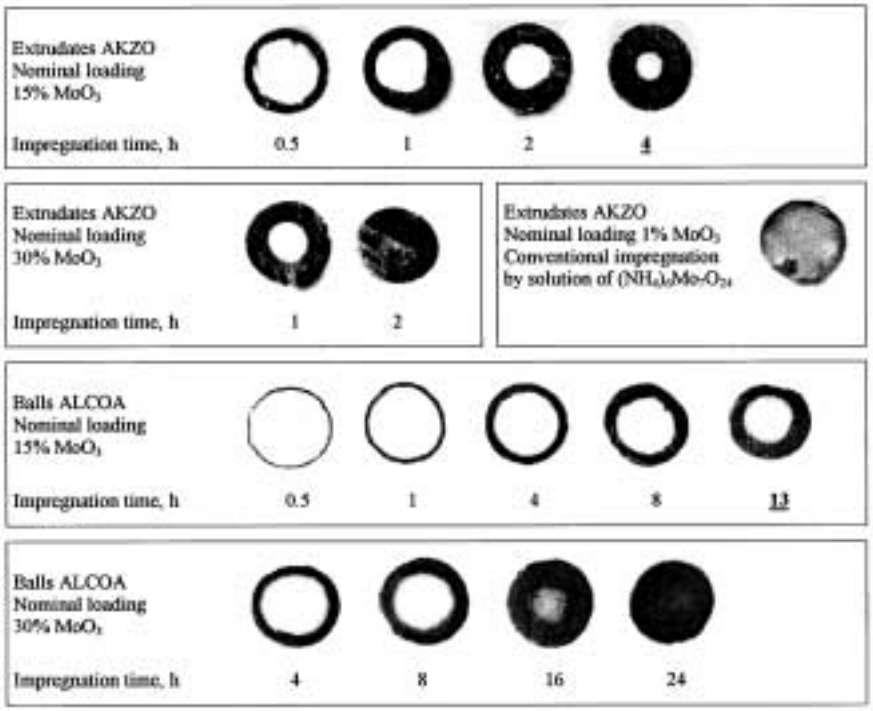

Figure 1. Mo concentration profiles evaluated by sulfidation of samples obtained by slurry impregnation at 100 °C using various nominal loadings and impregnation times. The bold and underlined value of impregnation time means that all MoO_3 disappeared from the slurry at that time. The 1% MoO_3 sample prepared by conventional impregnation is also included.

chemical potential of the last adsorbed species is equal to the chemical potential of solid MoO_3. The saturation adsorption Mo amount obtained corresponds to filled monolayer loading [7–9]. For nominal loadings of MoO_3 lower than or equal to the filled monolayer loading, all solid MoO_3 disappears from the slurry and the amount of dissolved Mo is negligible at the end of impregnation. No waste solution or slurry remains.

3.2. Comparison of Mo profile evaluation methods

It was found that the simple method of sulfidation of samples provides very useful information about Mo profiles. It is seen in figure 1 that a very low concentration of Mo was detected. The colour of the extrudates impregnated by 1% MoO_3 by conventional impregnation was grey across the whole extrudate. A sharp borderline of colour was observed for extrudates and balls impregnated by the SIM method. The interior of particles with various eggshell thickness was completely white (with the exception of fully or almost fully saturated samples), indicating zero or very small concentration of Mo.

However, the sulfidation does not provide quantitative information about the Mo concentration in the eggshell, and this information was obtained by EPMA. The data for Akzo extrudates and Alcoa balls are presented in figures 2 and 3, respectively.

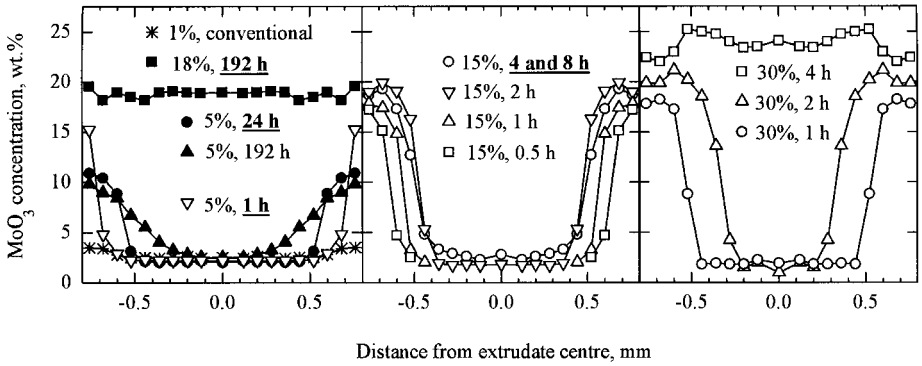

Figure 2. Mo concentration profiles evaluated by EPMA of samples obtained by slurry impregnation of Akzo extrudates using various nominal loadings, impregnation times and impregnation temperatures. The bold and underlined values of impregnation time means that all MoO_3 disappeared from the slurry at that time. Open and filled points are for impregnation temperatures of 100 and 25 °C, respectively. The 1% MoO_3 sample prepared by conventional impregnation is also included.

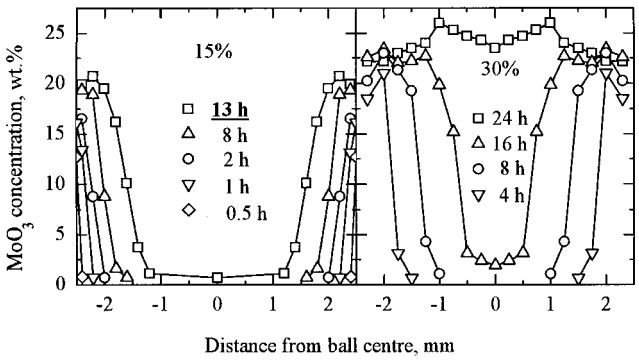

Figure 3. Mo concentration profiles evaluated by EPMA of samples obtained by slurry impregnation of Alcoa balls at 100 °C using various nominal loadings and impregnation times. The bold and underlined values of impregnation time means that all MoO_3 disappeared from the slurry at that time.

For slurry impregnated Alcoa balls, EPMA indicated practically zero Mo concentration in the interior of particles and that was in agreement with the completely white colour of the interior after sulfidation.

However, for slurry impregnated Akzo extrudates, EPMA indicated a small concentration of Mo of about 1.5–2% in the interior of particles even when the interior was completely white after sulfidation, For the catalyst with nominal loading of 1% MoO_3 prepared by conventional impregnation of Akzo extrudates EPMA indicated a content of MoO_3 of about 2–3%. All this means that EPMA slightly overestimated the Mo concentration in the Akzo extrudates. This is explained by the relatively high content of SO_4^{2-} ion of about 1.3 wt% in this alumina because the signals of S and Mo species coincide.

The thickness of the eggshell measured by EPMA, D_{EPMA}, can be defined as the width of the wave at half of the wave height. The thickness of the eggshell measured by the sulfidation method, D_{SULP}, is defined by the sharp borderline between black and white colours. The value of D_{SULP} was always higher than that of D_{EPMA} because even a very small Mo concentration at the diffuse front (foot) of the wave was detected by sulfidation.

3.3. Saturation adsorption loading obtained by slurry impregnation

3.3.1. Impregnation at 100 °C

The Area per Mo Atom at Filled Monolayer, AMAFM, in MoO_3/Al_2O_3 catalysts prepared by various methods was evaluated by several methods in the literature. Values in the range 0.20–0.35 nm^2 $atom^{-1}$ were reported, and the typical value was about 0.24 nm^2 $atom^{-1}$ (for a review see ref [9]). Using that value, the calculated filled monolayer loading is 21 and 22 wt% MoO_3 for the Akzo and Alcoa aluminas, respectively.

The filled monolayer loading was evaluated as saturated adsorption loading, SAL_{100}, in the present work using the nominal loading of 30 wt% MoO_3 and an impregnation temperature of 100 °C. It is shown in figures 2 and 3 that saturation (and an essentially uniform profile) was achieved after an impregnation time of 4 and 24 h for the Akzo extrudates and Alcoa balls, respectively. The difference in the time needed is connected with the difference in particle dimensions and with the difference in texture. The distance from the outer surface to the middle of a particle is more than 3 times longer for the balls than for the extrudates, Alcoa alumina possesses smaller pores and porosity than Akzo alumina (see Section 2.1).

The values of SAL_{100} determined by EPMA were about 22 and 24% for Akzo and Alcoa alumina, respectively (see data in figures 2 and 3 for samples with nominal loading of 30%; the value for Akzo alumina was lowered by 1.5% as the correction for the S signal), and those obtained by AAS were 18 and 20%, respectively. All these values reasonably well correspond to the above-mentioned calculated filled monolayer loadings using the value of AMAFM of 0.24 nm^2 $atom^{-1}$ (21 and 22%, respectively).

It is concluded, in agreement with our previous results with various other aluminas [7–9], that the filled monolayer density obtained by slurry impregnation with aluminas used in the present work is similar to values obtained for other aluminas and by other methods in the literature.

3.3.2. Impregnation at 25 °C

The slurry impregnation at 25 °C was considerably slower than at 100 °C. Only one experiment was performed to show that the support could be saturated even at room temperature. The SAL_{100} achieved for Akzo extrudates and evaluated by AAS was 18 wt% MoO_3 and that loading was selected for experiment at 25 °C. It is seen in figure 2 that all MoO_3 disappeared after 192 h and a uniform profile was achieved. The loading determined by EPMA (about 19%) was somewhat higher than the nominal loading of 18%, in agreement with the above conclusion that EPMA concentrations in Akzo extrudates were slightly overestimated.

3.4. Mo profiles achieved by slurry impregnation

3.4.1. Impregnation at 100 °C

The profiles obtained for various loadings and at various impregnation times are shown in figures 1–3. A sharp Mo concentration wave penetrating the support particles as the impregnation time is increased was observed both for extrudates and balls.

According to figures 2 and 3, the height of the wave increased only a little with impregnation time and it was close to saturation adsorption loading. Even with the low nominal loading of 5% the height of the wave was about 15% (figure 2). Adsorption was so strong under SIM conditions that practically all Mo species arriving into a particular distance inside the support

particle were adsorbed until the support saturation in that place.

It follows from figures 2 and 3 that the final position of the wave, that is, the shell thickness, can be controlled in two ways.

One possibility is to control the shell thickness by impregnation time. The impregnation is stopped at a given time needed for the required shell thickness (that time is estimated experimentally). The catalyst is separated from the unreacted MoO_3 by decantation. However, the disadvantage of this arrangement is that waste slurry remains after impregnation.

A more convenient possibility is to control the shell thickness by the nominal loading used. All MoO_3 in the slurry is consumed at the end of impregnation and no waste is produced. The dependence of the nominal loading needed for the required shell thickness D_{EPMA} was calculated assuming a rectangular shape of the wave and assuming that the height of the wave was equal to SAL_{100} (determined by EPMA), independently of the impregnation time. The curves obtained are plotted in figure 4. It is seen in figure 4 that the experimental values of D_{EPMA} obtained with several nominal loadings correspond well with the calculated curves.

The important result as to stability of profiles under impregnation conditions is seen in figure 2 for Akzo alumina and a nominal loading of 15%. All solid MoO_3 was consumed after 4 h and the heating of the mixture continued for an additional 4 h. The profile was not changed by this additional heating.

3.4.2. Impregnation at 25 °C

The possibility of achieving eggshell profiles at room temperature was tested with Akzo extrudates and nominal loading of 5%. All powder of MoO_3 disappeared after 24 h and the resulting profile was less sharp than at 100 °C (see figure 2). This suggests that adsorption at room temperature is weaker than at 100 °C. Surface OH groups are important for chemisorption of Mo species and higher temperature probably promotes full hydration of alumina surface. The reaction of Mo species with Al_2O_3 surface (chemisorption) at higher temperature may be accompanied by some "corrosion" of the alumina surface [10] and this "corrosion" may increase the capacity of alumina for chemisorption of Mo species.

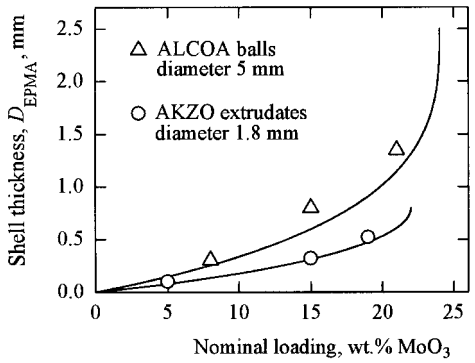

Figure 4. The regulation of the shell thickness by nominal loading. The lines were calculated using SAL_{100} of 22 and 24% for Akzo and Alcoa alumina respectively, The points are experimental data obtained at an impregnation temperature of 100 °C.

It was checked that the profile obtained after the disappearance of all MoO_3 powder (24 h) was rather stable under impregnation conditions. A very long impregnation time of 192 h was needed to achieve some diffusion broadening of the profile.

3.5. Hydrodesulfurization activity

It was found in previous papers for other aluminas (Sheralite [7], Norton [7,8], Condea [9]) that the HDS activity of SIM samples was the same or even slightly better than that of corresponding laboratory or industrial catalysts prepared by conventional impregnation. In order to confirm this also for the aluminas used in the present work (Akzo, Alcoa), the activity of the saturated adsorption samples (samples with uniform Mo profile in figures 2 and 3) was tested. The conversions x_{TH} were in the range of 10–90%, depending on catalyst and temperature. The curves x_{TH} *versus* temperature for individual catalysts did not cross mutually and the ranking of catalysts was practically independent of temperature.

It was checked previously that the dependencies of x_{TH} *versus* space time W/F_{TH} under the conditions of our test are well approximated by a pseudo first-order rate equation. The rate constants k were calculated from conversions at 400 and 340 °C and are shown in table 1.

Table 1
Relative HDS activity of MoO_3/Al_2O_3 catalysts. k(cat) and k(Mo) is the pseudo first-order rate constant normalized to gram of catalyst and gram of Mo, respectively. The reference catalyst r is commercial catalyst BASF M 8-30

Catalyst i	MoO_3 loading (wt%) [a]	$k(cat)_i/k(cat)_r$		$k(Mo)_i/k(Mo)_r$	
		400 °C	340 °C	400 °C	340 °C
Saturated Akzo alumina [b]	18	1.8	1.6	1.6	1.4
Saturated Alcoa alumina [c]	20	1.2	1.2	0.9	0.9
BASP M 8-30	15	1.0	1.0	1.0	1.0

[a] Determined by AAS.
[b] Nominal loading 30%, impregnation time 4 h.
[c] Nominal loading 30%, impregnation time 24 h.

It is seen that the activity of SIM catalysts is at least on the same level as that of commercial samples, in agreement with our previous experience mentioned above.

4. Conclusions

Reaction of alumina particles with slurry MoO_3/water is a simple and convenient method of preparation of MoO_3/Al_2O_3 catalysts with eggshell radial profile of Mo concentration. The profiles obtained are almost rectangular. The Mo concentration in the shell is practically independent of the shell thickness and is close to the filled monolayer loading. The shell thickness can be regulated by the amount of MoO_3 used. No waste solution or slurry is produced. A uniform profile is obtained when the amount of MoO_3 used corresponds to saturation adsorption loading, that is, to filled monolayer loading.

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