Catalysis Letters Vol. 112, Nos. 3–4, December 2006 (© 2006)
DOI: 10.1007/s10562-006-0202-z

Preparation of MoO_3/TiO_2 Catalysts with Eggshell and Uniform Mo Distribution by Water-Assisted Spreading of MoO_3

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Received 20 September 2006; accepted 5 October 2006

MoO_3/TiO_2 catalysts were prepared by reaction of TiO_2 extrudates (140 m^2g^{-1}) with a MoO_3/H_2O slurry. The adsorption of molybdena species was strong; sharp, deep eggshell profiles of the Mo concentration were obtained. The hydrodesulfurization activity of saturated catalysts with a uniform Mo distribution (about 10 wt.% MoO_3) was at least the same as that of a sample prepared by conventional impregnation.

KEY WORDS: MoO_3/TiO_2; eggshell catalysts; hydrodesulfurization; solvent-assisted spreading.

1. Introduction

Catalysts based on MoO_3/TiO_2 are active in various reactions of industrial importance such as hydrodesulfurization [1–3], partial oxidation of methanol [4], vapour-phase ammoxidation of toluene [5], the water–gas shift reaction [6], epoxidation of allylacetate with 3-butyl hydroperoxide [7], oxidation of 1-butene and butadiene [8] and selective catalytic reduction of NO_x by NH_3 [9–12].

MoO_3/TiO_2 catalysts are commonly prepared by impregnation of TiO_2 with a solution of $(NH_4)_6Mo_7O_{24}$ followed by calcination to remove ammonia. MoO_3 can also be deposited on TiO_2 by thermal spreading (solid-solid wetting), which consists in heating an intimate mechanical mixture of the two oxides at 450–500 °C [13, 14]. In the present work we have used a new method called solvent-assisted (or water-assisted) spreading.

We have previously used the method of water-assisted spreading for the preparation of MoO_3 supported on alumina [15, 16] and active carbon [17]. The support reacts with a MoO_3/H_2O slurry. The solubility of MoO_3 is low but sufficient for the gradual dissolution and adsorption of Mo species on the support surface. The pH of MoO_3/H_2O (2–2.8) is lower than the point of zero charge of alumina (6–8) and of active carbon (7–8). The support surface is positively charged and this promotes adsorption of molybdenum-containing anions. The adsorption is very strong and catalysts with deep, sharp eggshell profiles of the Mo concentration are obtained [16]. In the present work we have applied this method to the MoO_3/TiO_2 system.

Catalysts with an eggshell profile of the Mo concentration are of both theoretical and practical interest. Eggshell catalysts might find application when the catalysed reaction is fast and internal diffusion is the rate-determining step. The reaction product is transported from the eggshell structure more easily than from the interior of the catalyst particles, and undesired consecutive reactions are suppressed.

2. Experimental

2.1. Characterization of the support

The TiO_2 in the form of extrudates 3.2 mm in size was provided by Alpha Aesar, Germany (Cat. No 044429). Its BET surface area and the size distribution of the pores were measured by nitrogen physisorption using an ASAP2010 instrument (Micromeritics). The texture of the TiO_2 was compared with a typical Al_2O_3 support AKZO HDS-000-1.5 used for hydrodesulfurization catalysts.

2.2. Water-assisted spreading at 25 °C

The MoO_3 used was ground for 27 h in a planetary mill. A mixture of TiO_2 extrudates (15 g), MoO_3 (2.65 g) and water (40 ml) was left to stand and the samples of six extrudates were taken out at various time intervals. The samples were washed quickly with water and dried in a vacuum rotary evaporator. The eggshell profiles were visualized by two methods, namely sulfidation and electron probe microanalysis. At the end of impregnation, the unreacted slurry was separated from the remaining extrudates by decantation. The final extrudates were washed with water, dried and analysed for MoO_3 content; a value of 10.4 wt.% MoO_3 was

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obtained. The samples were not calcined. The unreacted slurry was dried and 1.158 g of solid was obtained, which contained 83% of MoO_3.

2.3. *Water-assisted spreading at 95 °C*

The impregnation mixture was heated under reflux condenser. Otherwise, the procedure was the same as at 25 °C. The content of MoO_3 in final remaining extrudates was 10.5 wt.% of MoO_3. The weight of the solid after drying the unreacted slurry was 1.196 g and the content of MoO_3 in it was 85%.

2.4. *Conventional impregnation*

The nominal content of MoO_3 was 10.5 % MoO_3, the same as the content of the final extrudates prepared by saturated solvent-assisted spreading as described above. The TiO_2 extrudates were crushed to 0.16–0.32 mm particle size. TiO_2 (5 g) was mixed with a solution of the corresponding amount of $(NH_4)_6Mo_7O_{24}$ and left to stand for 1 h. The mixture was dried in a vacuum rotary evaporator at 90 °C for 40 min. The catalyst was calcined in a fixed bed reactor in a stream of air: the temperature was increased by the rate of 15 °C min^{-1} to 400 °C and kept constant for 45 min.

2.5. *Reference catalyst*

The reference point of the activity was a commercial MoO_3/Al_2O_3 catalyst BASF M 8–30. Its MoO_3 content was 15 wt.% and its surface area was 210 m^2 g^{-1}.

2.6. *Visualization of eggshell catalysts by sulfidation*

The extrudates were sulfided with a H_2S/H_2 (1:10) mixture for 1 h at 400 °C. The sulfided extrudates were halved and the radial profiles were electronically scanned. With pure TiO_2 extrudates, we checked that the original pure white colour changed to pale grey after sulfidation. The colour of the parts of the extrudates containing adsorbed MoO_3 changed to black.

2.7. *Electron probe microanalysis*

The extrudates were halved, cemented with an instant adhesive into holes in a plastic disc and ground flush with a fine-toothed file. A JEOL JXA electron microscope, equipped with an EDAX PV 9400 analyser, was used. The average loading of squares of size $100 \times 100 \mu m$ were measured across the profile of the extrudates.

2.8. *Hydrodesulfurization activity*

The model reaction was the gas-phase hydrodesulfurization (HDS) of thiophene (TH) in a fixed-bed flow reactor at total pressure of 1 MPa. The feed rate of TH, F_{TH}, was 0.909 mmol h^{-1}, and that of hydrogen, F_{H2}, was 0.732 mol h^{-1}. The catalyst charge, W, was 0.035 g (0.16–0.32 mm particle size fraction). The catalyst was presulfided in situ by an H_2S/H_2 mixture (1:10) at atmospheric pressure using a temperature programme consisting of a ramp rate of 6 °C min^{-1} to 400 °C and a dwell time of 1 h at 400 °C. The TH/H_2 feed was introduced at a temperature of 400 °C and a pressure of 1 MPa. The TH conversion, x_{TH}, was determined at several temperatures from 400 to 280 °C, at temperature steps of 30 °C. The conversion was defined as $x_{TH} = (n°_{TH} - n_{TH})/n°_{TH}$, where $n°_{TH}$ and n_{TH} are the initial and final number of moles of thiophene, respectively. The values were in the range 0.02–0.85, depending on catalyst and temperature. The test lasted about 9 h and no significant deactivation was observed.

It was checked with the commercial MoO_3/Al_2O_3 catalyst that the reaction followed a pseudo-first-order rate kinetic equation under our conditions. In these experiments, six catalyst charges were tested, and the curve $x_{TH} = f(W/F_{TH})$ followed well the integrated pseudo-first-order rate equation for the range of conversion values 0–0.9. The activity of the catalyst was evaluated as the pseudo-first-order rate constant, with dimension $mmol_{TH}\ g_{cat}^{-1}\ h^{-1}$.

3. Results and discussion

3.1. *Characterization of the support*

Nitrogen adsorption isotherms of TiO_2 and a typical Al_2O_3 support are shown in figure 1. The samples exhibited Type IIb and IVa isotherms, respectively, characteristic of mesoporous solids [18]. The hysteresis loop of TiO_2 was less pronounced than that of Al_2O_3. The BET surface area was 140 and 262 cm^3 g^{-1}, respectively, the volume of pores was 0.33 and 0.60 cm^3 g^{-1}, respectively, and the volume of micropores was 0.001 and 0.01 cm^3 g^{-1}, respectively. It can be concluded that the capacity of our TiO_2 for MoO_3 dispersion was lower than that of typical Al_2O_3.

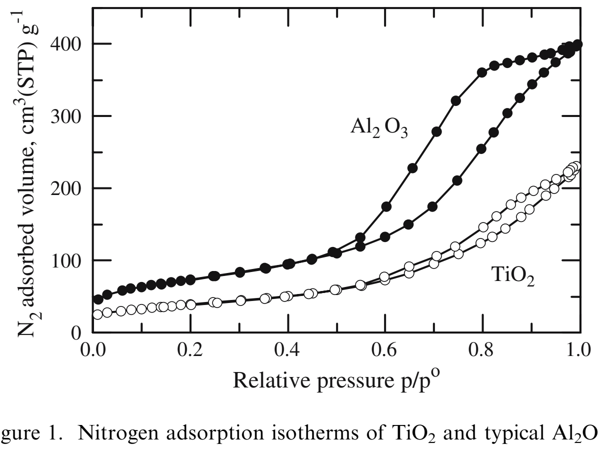

Figure 1. Nitrogen adsorption isotherms of TiO_2 and typical Al_2O_3.

3.2. Eggshell profiles

The results are presented in figure 2. It can be seen that sharp, deep Mo concentration profiles are formed. The MoO_3 concentration in the eggshell is high, about 9–10 wt.%. The content of MoO_3 in the saturated extrudates with a uniform MoO_3 distribution was about 10%, which agrees well with the values obtained by AAS analysis (see the Experimental section). This value corresponds to the density of a saturated monolayer, 3.3 atoms Mo per 1 nm^2. This is similar to the value of 3.4 atoms Mo nm^{-2} that we obtained with the MoO_3/Al_2O_3 system [15].

The impregnation at 95 °C was considerably faster than at 25 °C. Uniform saturation of the whole extrudates was already achieved after 45 h at the increased temperature whereas, a shell of about 0.6 mm thick was obtained at 25 °C after 52 h. However, the high temperature caused cracking of some extrudates.

The formation of sharp, deep profiles is caused by the very strong adsorption of molybdena species under the conditions of solvent-assisted spreading. The pH of the MoO_3/H_2O slurry used for impregnation was about 2.1, and the point of zero charge of our TiO_2 was about 5.5. The surface is positively charged under the conditions used and that is the driving force for the strong adsorption of molybdenum containing anions.

3.3. Hydrodesulfurization activity

It can be seen from Table 1 that the activity of the MoO_3/TiO_2 prepared by conventional impregnation was considerably higher than that of the reference commercial Al_2O_3 supported sample. This is in agreement with the results of previous studies [1, 3, 19, 20].

Table 1

Hydrodesulfurization activity of MoO_3/TiO_2 catalysts

Catalyst preparation	Content of MoO_3, wt.%	Rate constant, $mmol_{TH}\ g_{cat}^{-1}\ h^{-1}$	
		370 °C	340 °C
Conventional impregnation of TiO_2	10.5	22.0	10.4
Solvent-assisted spreading at 25 °C	10.4	24.9	11.1
Solvent-assisted spreading at 95 °C	10.5	24.1	10.7
Reference commercial MoO_3/Al_2O_3	15.0	15.5	8.0

The final uniformly saturated extrudates were crushed to 0.16–0.32 mm particle size and the activity of these samples was compared with the activity of the catalyst prepared by conventional impregnation. The results are also shown in Table 1. It can be seen that the samples obtained by solvent-assisted spreading were at least as active as the conventional sample. This means that good dispersion of molybdena species was achieved by solvent assisted spreading.

4. Conclusions

The MoO_3/TiO_2 catalysts with a sharp, deep eggshell Mo concentration profiles have been prepared by solvent-assisted spreading, that is by the reaction of TiO_2 extrudates with an MoO_3/H_2O slurry. The MoO_3 concentration in the shell is close to that of a saturated adsorbed monolayer. The thickness of the shell can be regulated either by the reaction time or by the amount of MoO_3 used. The hydrodesulfurization activity of the

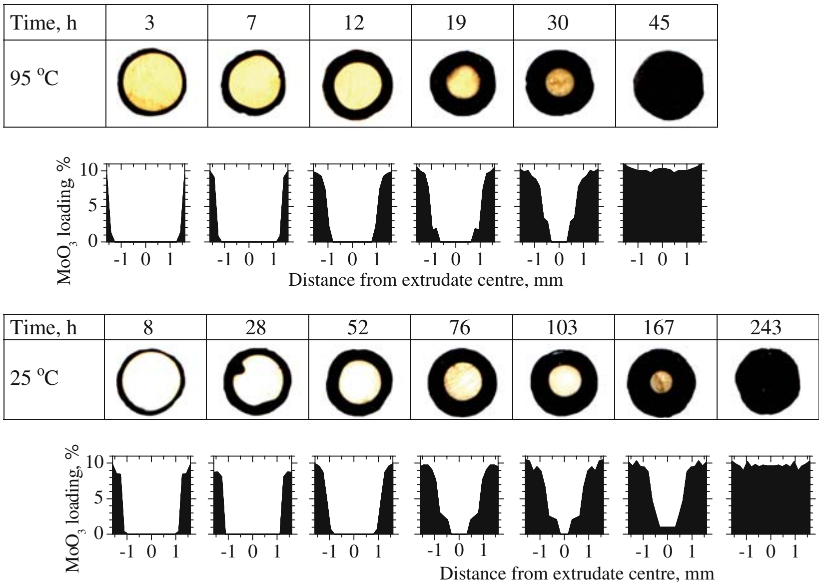

Figure 2. Development of eggshell structure during water-assisted spreading. The structure was visualized by sulfidation and the Mo concentration was measured by electron probe microanalysis.

active phase deposited by solvent-assisted spreading is at least the same as of a phase deposited by conventional impregnation.

Acknowledgments

Financial support from the Grant Agency of the Czech Republic is gratefully acknowledged (Grant No. 104/06/0705).

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