

## Tailored Distribution of MoO<sub>3</sub> in the TiO<sub>2</sub> and ZrO<sub>2</sub> Supported Catalysts by Water-Assisted Spreading

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### Abstract

A new method for preparation of both eggshell and uniformly distributed MoO<sub>3</sub> in titania and zirconia supported catalysts was studied. Spreading of MoO<sub>3</sub> onto the supports in water was followed by electron probe microanalysis and visually after sulfidation. Eggshell type distribution with saturation adsorption loading 3.3 and 3.2 Mo atoms per nm<sup>2</sup> of TiO<sub>2</sub> and ZrO<sub>2</sub> was formed before the uniform distribution was reached. The thickness of the eggshell was found to be easily controlled either by MoO<sub>3</sub> amount used for the spreading or by reaction time. The uniformly saturated catalysts MoO<sub>3</sub>/TiO<sub>2</sub> and MoO<sub>3</sub>/ZrO<sub>2</sub> were tested in hydrodesulfurization of thiophene and benzothiophene in their sulfidic states. They exhibited the same hydrodesulfurization activity and relative selectivity hydrogenation/hydrogenolysis as their counterparts prepared by conventional impregnation from solution of ammonium heptamolybdate, which confirmed good dispersion of Mo species achieved by water-assisted spreading method.

Keywords: eggshell catalysts, solvent-assisted spreading, hydrodesulfurization, MoO<sub>3</sub>/TiO<sub>2</sub>, MoO<sub>3</sub>/ZrO<sub>2</sub>

### 1. Introduction

MoO<sub>3</sub> supported on TiO<sub>2</sub> and ZrO<sub>2</sub> is widely studied catalysts' precursor because of its usage in variety of industrially important reactions, such as hydrodesulfurization (HDS) [1–11], the water-gas shifts [12], ammoxidation of toluene [13,14] and partial oxidation of methanol [15,16]. MoO<sub>3</sub>/TiO<sub>2</sub> catalysts, moreover, exhibited activity in epoxidation of allyl acetate with tert.-butyl hydroperoxide [17], oxidation of 1-butene and butadiene [18], and selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> [19–22]. MoO<sub>3</sub>/ZrO<sub>2</sub> catalysts, furthermore, were found to be active in the hydrogenation of carbon monoxide and toluene [23], the hydrogenation and metathesis of propene [24], oxidative dehydrogenation of propane [25], heptane isomerisation [26], toluene benzoylation with benzoic anhydride [27],

2-propanol dehydration and cumene dealkylation [28], 2-butanol dehydration and esterification of acetic acid with ethanol [29], methane oxidation [30,31], epoxidation of propylene [32,33], and ammoxidation of 3-picoline [34].

MoO<sub>3</sub>/TiO<sub>2</sub> and MoO<sub>3</sub>/ZrO<sub>2</sub> catalysts are usually prepared by impregnation of support with an aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> followed by calcination to remove ammonia. That method, in this paper, was called conventional impregnation method (CIM). MoO<sub>3</sub> can also be deposited onto oxidic supports by so called thermal spreading method (TSM), which is an heating of an intimate mechanical mixture of MoO<sub>3</sub> with support at 450–500 °C [35,36]. In the present work, we have used a new method, called water-assisted spreading method (WSM). MoO<sub>3</sub> was allowed to react with (spread over) the supports TiO<sub>2</sub> and ZrO<sub>2</sub> in aqueous slurries. Similar approach has already been applied for preparation of MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [37,38] and MoO<sub>3</sub>/C [39] catalysts. The solubility of MoO<sub>3</sub> was low but sufficient for the gradual dissolution and adsorption of Mo species on the support surface. The pH of MoO<sub>3</sub>/H<sub>2</sub>O (2–2.8) was lower than the points of zero charge of alumina (6–8) and of activated carbon (7–8). The support surface was positively charged, and this enhanced adsorption of anionic molybdenum species. The adsorption was very strong, and catalysts with deep, sharp eggshell profiles of the Mo concentration were obtained [38,40].

A controlled distribution of MoO<sub>3</sub>, eggshell/uniform, in the TiO<sub>2</sub> and ZrO<sub>2</sub> is both of theoretical and practical interest. The eggshell catalysts find application when a rate-determining step is internal diffusion. A desirable reaction product is transported from the eggshell structure more easily than from the interior of the catalyst particles preventing it from further and unwanted consecutive reactions. The aim of this work was to find out whether the water-assisted spreading of MoO<sub>3</sub> proceeds over pre-shaped TiO<sub>2</sub>, ZrO<sub>2</sub> and ZrO(OH)<sub>2</sub> supports and leads to desirable eggshell Mo distribution as was the case for Al<sub>2</sub>O<sub>3</sub>. The supports were characterised by powder x-ray diffraction, point of zero charge (PZC), nitrogen physisorption, and the deposited Mo species by hydrodesulfurization reaction of thiophene and benzothiophene.

## **2. Experimental**

### **2.1. Supports**

TiO<sub>2</sub> (AlfaAesar, product no. 044429) and ZrO<sub>2</sub> (AlfaAesar, product no. 43815) extrudates possessed external diameter 3.2 mm and an average length 8 mm. ZrO(OH)<sub>2</sub> (MEL Chemicals) extrudates with external diameter 3 mm and average length 10 mm contained of about 15 wt.% of Al<sub>2</sub>O<sub>3</sub> as a binder.

### **2.2. Water-assisted spreading**

The MoO<sub>3</sub> (Fluka, product no. 69850) was ground 24 h in a planetary mill before use. A mixture consisted of 15 g of support extrudates, 6.43 g of MoO<sub>3</sub> and 50 ml of H<sub>2</sub>O was heated under reflux condenser at 95 °C and the samples of six extrudates were taken out at various time intervals. The samples were washed with water and dried in a vacuum evaporator at 100 °C. At the end of spreading, the unreacted slurry was separated from the remaining extrudates by decantation. The final extrudates were dried and analysed for MoO<sub>3</sub> content by atomic absorption

spectroscopy (AAS); final value 10.5, 7.6, and 20.8 wt.% was obtained over TiO<sub>2</sub>, ZrO<sub>2</sub>, and ZrO(OH)<sub>2</sub> extrudates, respectively.

Additionally, the ZrO(OH)<sub>2</sub> was allowed to react with MoO<sub>3</sub>/H<sub>2</sub>O slurry at 25 and 95 °C. Three nominal loadings of MoO<sub>3</sub> 5, 10, and 15 wt.% (per solid part of the mixtures) were used. At the end of the water-assisted spreading, all the MoO<sub>3</sub> disappeared from the mixtures and the extrudates were dried in a vacuum evaporator at 100 °C. Actual content of MoO<sub>3</sub> in the final catalysts was analysed by AAS and was the same as the nominal one.

### 2.3. Conventional impregnation

TiO<sub>2</sub>, ZrO<sub>2</sub>, and ZrO(OH)<sub>2</sub> extrudates were crushed and sieved to particle size 0.15-0.32 mm and impregnated with aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> for 1 h, in which the nominal content of MoO<sub>3</sub>, calculated per solid part of the impregnation mixture, was 10.5, 7.6, and 20.8 wt.%, respectively. Then the grains were evacuated in a vacuum evaporator, dried there at 100 °C for 1 h, and calcined in a fixed bed tubular reactor in a stream of air with a ramp rate 15 °C min<sup>-1</sup> and a dwell time of 0.5 h at 400 °C.

### 2.4. Point of zero charge

The point of zero charge (PZC) was measured by simplified mass titration method [41] with a WTW pH meter equipped with a cell Hamilton Slimtrode. The PZC of selected samples was also obtained from a plot of zeta potential versus pH (2-9). The zeta potential was measured with Coulter Delsa 440 SX (Coulter Electronic, USA). Prior the measurement, pH of each sample (0.04 g of solid sample and 40 ml of water) was adjusted with NaOH or HCl.

### 2.5. Nitrogen physisorption

N<sub>2</sub> adsorption isotherms were measured with a Micromeritics ASAP 2010M instrument. Prior to these measurements, the samples were evacuated at 110 °C for 12 h. Specific surface area (S<sub>BET</sub>) was determined by the common Brunauer, Emmett und Teller (BET) procedure.

### 2.6. Powder x-ray diffraction

Powder x-ray diffraction data were collected on a Philips X'Pert MPD system using CuKα radiation (40 kV, 40 mA) and a secondary graphite monochromator. Data were collected in the range of 10–70° 2 theta and the rate of measurement was 0.03° per 3 s.

### 2.7. Evaluation of eggshell distribution

Visualization of the Mo eggshell were done via sulfidation of the extrudates with an H<sub>2</sub>S/H<sub>2</sub> (1:10) mixture for 1 h at 400 °C. The sulfided extrudates were halved and the radial profiles were electronically scanned. With pure 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<sub>3</sub> changed to black.

Electron probe microanalysis (EPMA) was done on a JEOL JXA electron microscope, equipped with an EDAX PV 9400 analyser over the extrudates, which

were halved, cemented with an instant adhesive into holes in a plastic disc and ground flush with a fine-toothed file. The average loading of prism of size  $100 \times 100 \times 1 \mu\text{m}$  were measured across the profile of the extrudates.

## 2.8. Hydrodesulfurization

Benzothiophene (BT) hydrodesulfurization (HDS) was carried out in the gas phase in a fixed-bed tubular-flow microreactor (i.d. 3 mm). The composition of the starting reaction mixture was kept constant and it contained 16, 200 and 1384 kPa of BT, decane and hydrogen, respectively. The catalyst charge was varied from 0.1 to 0.5 g, depending on its activity, and was diluted with inert  $\alpha\text{-Al}_2\text{O}_3$  to form a bed length of 30 mm. The reaction was run at 360 °C and at three feed rates of BT: 7.7, 10.3 and 15.5 mmol h<sup>-1</sup>. Steady-state was reached in 20 min after each change of the feed rate, and deactivation of the catalysts was not observed. The reaction mixture was analysed on a Hewlett-Packard gas chromatograph (6890 series). The reaction products were dihydrobenzothiophene (DHBT) and ethylbenzene (EB). The following parameters were determined: relative composition of the reaction mixture,  $a_i$ , ( $a_{\text{BT}} = n_{\text{BT}}/n_{\text{BT}}^0$ ,  $a_{\text{DHBT}} = n_{\text{DHBT}}/n_{\text{BT}}^0$ ,  $a_{\text{EB}} = n_{\text{EB}}/n_{\text{BT}}^0$ ), or conversion,  $x_i$ ; overall conversion of BT ( $x_{\text{BT}} = 1 - a_{\text{BT}}$ ); conversion of BT to DHBT ( $x_{\text{DHBT}} = a_{\text{DHBT}}$ ) and conversion of BT to EB ( $x_{\text{EB}} = a_{\text{EB}}$ ), where  $n^0$  and  $n$  were the initial and final numbers of moles, respectively. Prior to the measurements, the catalysts were presulphided in situ in a H<sub>2</sub>S/H<sub>2</sub> flow (1/10) at a temperature ramp of 10 °C min<sup>-1</sup> to 400 °C and a dwell time of 1 h.

Thiophene HDS was carried out in the gas phase in a in a fixed-bed tubular-flow microreactor (i.d. 2 mm) at 370 °C, at a total pressure of 1 MPa. Thiophene conversion,  $x_{\text{TH}}$ , was defined as  $x_{\text{TH}} = (n_{\text{TH}}^0 - n_{\text{TH}})/n_{\text{TH}}^0$ , where  $n_{\text{TH}}^0$  and  $n_{\text{TH}}$  were the initial and final number of moles of thiophene, respectively. Further details can be found elsewhere [40].

The commercial catalysts Mo/Al<sub>2</sub>O<sub>3</sub> (BASF, Germany, M8-30) containing 15.0 wt.% of MoO<sub>3</sub> was used as a reference in both HDS reactions.

## 3. Results and discussion

### 3.1. Characterization of the supports

The nitrogen adsorption-desorption isotherm of the supports are shown in Fig. 1. TiO<sub>2</sub> and ZrO<sub>2</sub> exhibited a type IV N<sub>2</sub> adsorption isotherm [42], which is typical for materials containing mesopores, such as  $\gamma\text{-Al}_2\text{O}_3$ , while ZrO(OH)<sub>2</sub> was microporous with a type I isotherm similar to activated carbons [39]. The  $S_{\text{BET}}$  the supports are given in Table 1. It is seen that both unhydrous oxidic supports had considerably lower  $S_{\text{BET}}$  than the reference catalyst supported on Al<sub>2</sub>O<sub>3</sub> while hydrous zirconia possessed the highest  $S_{\text{BET}}$ .

An example of determination of a PZC from a plot of zeta potential versus pH is shown in Fig. 2 and the determined PZCs of the supports are summarised in Table 1. It was found that PZC received by simplified mass titration method is systematically shifted to higher values than that determined from plots of zeta potentials.

Table 1: Properties of the supports, catalysts with uniform and saturated loading of MoO<sub>3</sub> and commercial reference catalyst BASF M8-30

Sample	S <sub>BET</sub> , m <sup>2</sup> g <sup>-1</sup>	PZC*	PZC**
TiO <sub>2</sub>	140	5.5	5.0
MoO <sub>3</sub> (WSM)/TiO <sub>2</sub>	138	2.3	2.0
ZrO <sub>2</sub>	108	7.3	6.0
MoO <sub>3</sub> (WSM)/ZrO <sub>2</sub>	102	2.4	2.5
ZrO(OH) <sub>2</sub>	311	8.0	6.0
MoO <sub>3</sub> (WSM)/ZrO(OH) <sub>2</sub>	217	2.6	2.8
MoO <sub>3</sub>	-	2.1	-
MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> BASF	210	5.0	-

\* measured by simplified mass titration method

\*\* obtained from the graph of zeta potential versus pH (Fig. 2)

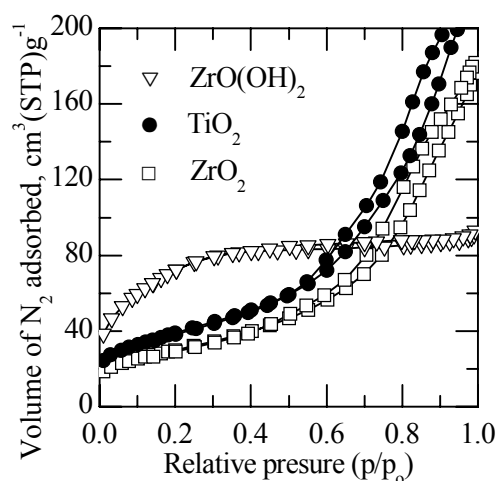


Figure 1: Nitrogen adsorption isotherms of the supports used

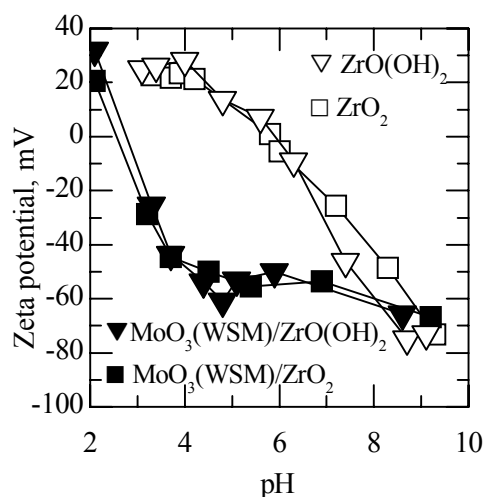


Figure 2: Example of the dependence of zeta potential on pH

Table 2: Hydrodesulfurization activity and relative selectivity to DHBT of the catalysts with uniform and saturated loading of MoO<sub>3</sub> and commercial reference catalyst BASF M8-30

Catalyst	Content of MoO <sub>3</sub> , wt. %	HDS of thiophene		HDS of benzothiophene	
		k <sub>TH</sub> , mmol <sub>TH</sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	k <sub>EB</sub> , mmol <sub>EB</sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	x <sub>DHBT</sub> at x <sub>BT</sub> =0.5	
MoO <sub>3</sub> (CIM)/TiO <sub>2</sub>	10.5	22.0	29.1	0.273	
MoO <sub>3</sub> (WSM)/TiO <sub>2</sub>	10.5	24.1	39.5	0.271	
MoO <sub>3</sub> (CIM)/ZrO <sub>2</sub>	7.6	15.5	27.0	0.270	
MoO <sub>3</sub> (WSM)/ZrO <sub>2</sub>	7.6	15.9	30.0	0.245	
MoO <sub>3</sub> (CIM)/ZrO(OH) <sub>2</sub>	20.8	3.7	5	-	
MoO <sub>3</sub> (WSM)/ZrO(OH) <sub>2</sub>	20.8	3.5	6	-	
MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> BASF	15.0	15.5	29.0	0.229	

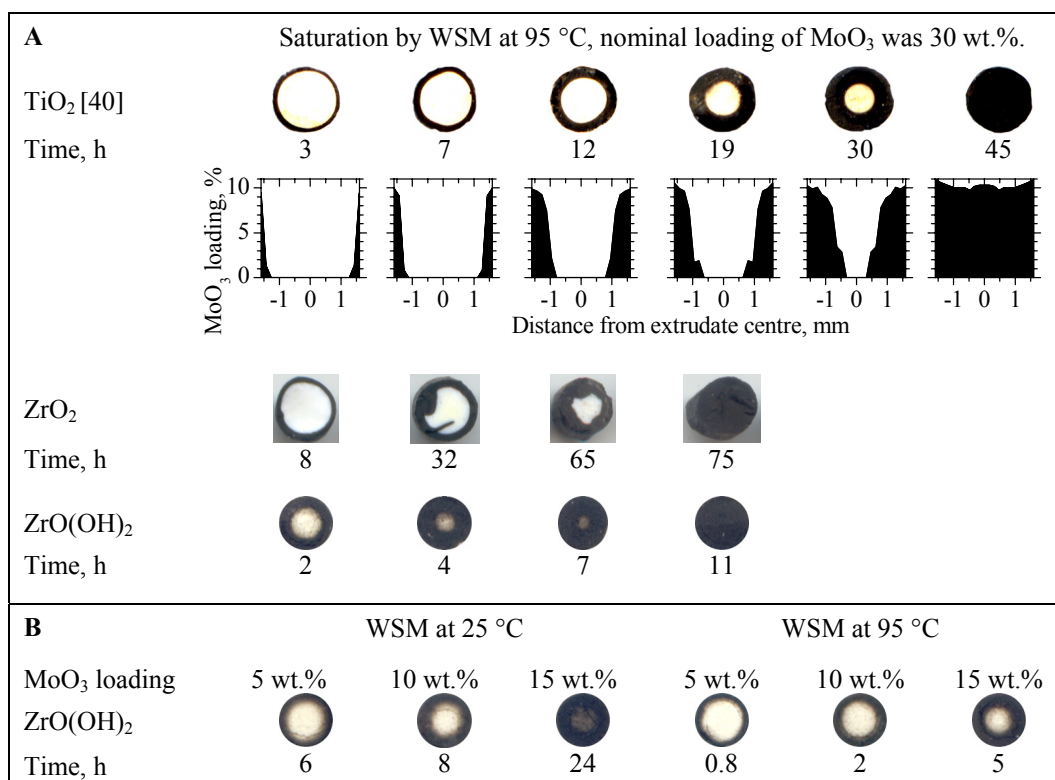


Figure 3: Development of eggshell structure during water-assisted spreading.

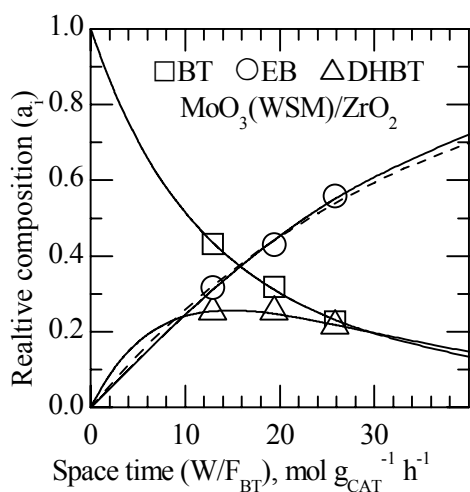


Figure 4: HDS of benzothiohene. Dashed line: fitting of  $k_{EB}$ .

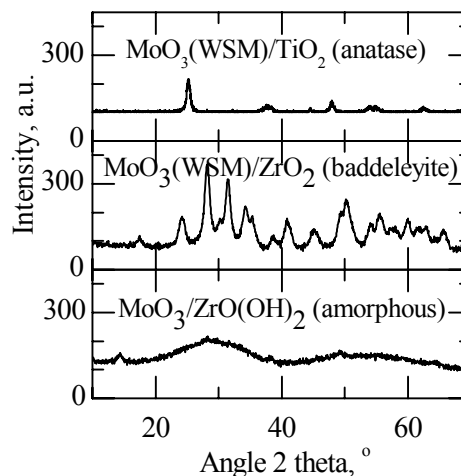


Figure 5: X-ray diffraction patterns (in brackets: determined phase).

Nevertheless, it was concluded that PZCs of all the supports were roughly close to 7 and thus close to the value reported before for alumina [37] and activated carbon [39].

### 3.2. Concept of MoO<sub>3</sub> deposition and formation of the eggshell

It was found that PZCs of all the supports used were well above the pH of the aqueous slurry of MoO<sub>3</sub>, which was about 2.1. The supports surfaces were therefore charged positively [43] and an adsorption of dissolved anionic species of MoO<sub>3</sub> was promoted. The dissolved species penetrated the pellets of support, gradually adsorbed there to form saturated adsorption monolayer of MoO<sub>3</sub>. After filling that monolayer, the impregnation continued deeper into the carrier up to the point where uniform distribution throughout the extrudates was achieved. The saturated adsorption loadings in the extrudates with uniform Mo distribution were determined by AAS and corresponded to the monolayer density of 3.3, 3.2, and 3.5 atoms Mo per nm<sup>2</sup> of TiO<sub>2</sub>, ZrO<sub>2</sub>, and ZrO(OH)<sub>2</sub> respectively, which was close to the value 3.4 atoms Mo.nm<sup>-2</sup> obtained previously with MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> systems [37]. Furthermore, formation of these uniform and saturated adsorption monolayer was also demonstrated by significant decrease in the extrudates PZCs (Table 1 and Fig. 1). The catalysts PZCs (2-2.8) were practically as low as the PZC of the unsupported MoO<sub>3</sub>.

The formation of the Mo eggshell was followed by EPMA and visually after sulfidation. The results are given in Fig. 3. Due to the fact that signal of Mo and Zr overlapped in EPMA, this method was not used for quantitative analysis in the case of Zr containing pellets. Nevertheless, the depth of Mo penetration observed visually qualitatively well correlated with EMPA. Further details of EMPA over TiO<sub>2</sub> extrudates can be found elsewhere [40].

It was found that a rate of water-assisted spreading decreased in order ZrO(OH)<sub>2</sub> > TiO<sub>2</sub> > ZrO<sub>2</sub>. For example, uniform Mo saturation over the support ZrO(OH)<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> was achieved after 11, 45, and 75 h of heating at 95 °C, respectively. Because the dimensions of all the extrudates used were similar as well as their PZCs, the only factor that might influence the rate of WSM was their S<sub>BET</sub>, which significantly decreased in the same order.

In general, the depth of Mo eggshell can be easily regulated by two ways: by time of spreading or by nominal amount of MoO<sub>3</sub>. From practical point of view, the latter is the method of choice. To demonstrate its feasibility, the selected nominal loadings were used to saturate ZrO(OH)<sub>2</sub> in Fig. 3 B. All the MoO<sub>3</sub> adsorbed at time given and distinct eggshells were formed.

### 3.3. Hydrodesulfurization activity

HDS activities of the catalysts with uniform Mo distribution and reference catalyst were determined after they were crushed and sieved to the particles size fraction 0.15-0.32 mm and were listed in Table 2. Thiophene hydrodesulfurized directly to C4 fraction and H<sub>2</sub>S and so the pseudo-first-order rate constant k<sub>TH</sub> describing the conversion of thiophene was used as an activity index. HDS of benzothiophene, however, can be described by a parallel consecutive scheme of four pseudo-first-order reactions (BT to DHBT, DHBT to BT, BT to EB and DHBT to EB), in which none of the four rate constants represented a proper index of overall HDS activity. For that reason, a formal pseudo-first-order rate constant, k<sub>EB</sub>,

describing the formation of EB, was fitted to use it as the activity index. An example of the  $k_{EB}$  fitting is given in Fig. 4. Furthermore, the conversion to hydrogenation intermediate DHBT ( $x_{DHBT}$ ) at 50% conversion of BT was chosen as an index of the relative selectivity C=C hydrogenation/ C-S hydrogenolysis (HYD/HYG). The HYD/HYG selectivity is an important parameter of evaluation of HDS catalysts [5] as it is believed that it refers on quality of active sites.

It was found that the activity of Mo deposited over  $TiO_2$  and  $ZrO_2$  by water-assisted spreading method (WSM) was slightly higher than that obtained with deposition by conventional impregnation method (CIM). Moreover, both methods of deposition led to practically the same HYD/HYG selectivity ( $x_{DHBT}$ ) in HDS of benzothiophene. These again confirmed that water-assisted spreading leads to good dispersion of Mo species. Predictably, it was found that  $MoO_3(WSM)/TiO_2$  and  $MoO_3(WSM)/ZrO_2$  exhibited intrinsic activities about 1.9 and 2.1 times higher, respectively, than that of the reference catalysts BASF, which is a typical  $\gamma$ -alumina supported catalyst. Similar results have been reported in the literature [8,9,11].

The activities of  $MoO_3(WSM)/ZrO(OH)_2$  and  $MoO_3(CIM)/ZrO(OH)_2$ , however, were extremely low despite the high Mo loading. Quite recently, we have found that the key factor that influenced the HDS activity of zirconia-supported phase could be the crystallographic structure of zirconia. X-ray diffraction patterns of the prepared samples are given in Fig. 5 as an illustration. Obviously, only the monoclinic form of  $ZrO_2$  led to high activity of deposited Mo not the amorphous one of  $ZrO(OH)_2$ . Further discussion can be found elsewhere [44].

#### **4. Conclusions**

$MoO_3/TiO_2$  and  $MoO_3/ZrO_2$  catalysts with a sharp, deep eggshell Mo concentration profile have been prepared by water-assisted spreading method, that is, by the reaction of  $TiO_2$  and  $ZrO_2$  extrudates with an  $MoO_3/H_2O$  slurry. The  $MoO_3$  adsorption monolayer in uniformly saturated extrudates exhibited surface density 3.3, 3.2 atoms Mo per  $nm^2$  of  $TiO_2$  and  $ZrO_2$ , respectively. 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 active phase deposited by water-assisted spreading is at least the same as of a phase deposited by conventional impregnation.

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## References

- [1] Duchet, J.C., Tilliette, M.J., Cornet, D., Vivier, L., Perot, G., Bekakra, L., Moreau, C. and Szabo G., (1991) *Catalysis Today*, 10, 579-592.
- [2] Weissman, J.G., Ko, E.I. and Kaytal, S., (1993) *Applied Catalysis A*, 94, 45-59.
- [3] Vrinat, M., Hamon, D., Breysse, M., Durand, B. and des Courieres, T., (1994) *Catalysis Today*, 20, 273-282.
- [4] Afanasiev, P., Geantet, C. and Breysse, M., (1995) *Journal of Catalysis*, 153, 17-24.
- [5] Orozco, E.O. and Vrinat, M., (1998) *Applied Catalysis*, 170, 195-206.
- [6] Pizzio, L., Vázquez, P., Cáceres, C. and Blanco, M., (1999) *Studies in Surface Science and Catalysis*, 127, 413-420.
- [7] Maity, S.K., Rana, M.S., Srinivas, B.N., Bej, S.K., Murali Dhar, G. and Prasada Rao, T.S.R., (2000) *Journal of Molecular Catalysis A*, 153, 121-127.
- [8] Breysse, M., Afanasiev, P., Geantet, C. and Vrinat, M., (2003) *Catalysis Today*, 86, 5-16.
- [9] Ji, Y., Afanasiev, P., Vrinat, M., Wenzhao Li and Can Li, (2004) *Applied Catalysis A*, 257, 157-164.
- [10] Maity, S.K., Rana, M.S., Bej, S.K., Ancheyta-Juárez, J., Murali Dhar, G. and Prasada Rao T.S.R., (2001) *Applied Catalysis A*, 205, 215-225.
- [11] Dzwigaj, S., Louis, C., Breysse, M., Cattenot, M., Belière, V., Geantet, C., Vrinat, M., Blanchard, P., Payen, E., Inoue, S., Kudo, H. and Yoshimura, Y., (2003) *Applied Catalysis B*, 41, 181-191.
- [12] Łaniecki, M., Małecka-Grycz, M. and Domka, F., (2000) *Applied Catalysis A*, 196, 293-303.
- [13] Chary, K.V.R., Reddy, K.R. and Kumar, Ch.P., (2001), *Catalysis Communication*, 2, 277-284.
- [14] Chary, K.V.R., Reddy, K.R., Kishan, G., Niemantsverdriet, J.W. and Mestl, G., (2004) *Journal of Catalysis*, 226, 283-291.
- [15] Brückman, K., Grzybowska, B., Che, M. and Tatibouët, J.M., (1993) *Applied Catalysis A*, 96, 279-288.
- [16] Kim, D.S., Wachs, I.E. and Segawa, K., (1994) *Journal of Catalysis*, 146, 268-277.
- [17] Kanai, H., Ikeda, Y. and Imamura, S., (2003) *Applied Catalysis A*, 247, 185-191.
- [18] Vanhove, D., Op, S.R., Fernandez, A. and Blanchard, M., (1979) *Journal of Catalysis*, 57, 253-263.
- [19] Fountzoula, Ch., Spanos, N., Matralis, H.K. and Kordulis, Ch., (2002) *Applied Catalysis B*, 35, 295-304.
- [20] Nova, I., Lietti, L., Casagrande, L., Dall'Acqua, L., Giamello, E. and Forzatti, P., (1998) *Applied Catalysis B*, 17, 245-258.
- [21] Bourikas, K., Fountzoula, Ch. and Kordulis, Ch., (2004) *Applied Catalysis B*, 52, 145-153.
- [22] Matralis, H., Theret, S., Bartians, P., Ruwet, M. and Grange, P., (1995) *Applied Catalysis B*, 5, 271-281.
- [23] Reyes, P., Fernández, J., Concha, I. and Pecchi, G., (1995) *Catalysis Letters*, 34, 331-341.

- [24] Indovina, V., Cimino, A., Cordischi, D., Della Bella, S., De Rossi, S., Ferraris, G., Gazzoli, D., Occhiuzzi, M. and Valigi, M., (1993) *Studies in Surface Science and Catalysis*, 75, 875-887.
- [25] Chen, K., Xie, S., Iglesia, E. and Bell, A.T., (2000) *Journal of Catalysis*, 189, 421-430.
- [26] Yori, J.C., Pieck, C.L. and Parera, J.M., (2000) *Catalysis Letters*, 64, 141-146.
- [27] Hino, M. and Arata, K., (1989) *Chemistry Letters*, 6, 971-972.
- [28] Sohn, J.R., Lee, S.G. and Shin, D.C., (2006) *Bulletin of Korean Chemical Society*, 27, 1623-1632.
- [29] Li, L., Yoshinaga, Y. and Okuhara, T., (2002) *Catalysis Letters*, 83, 231-234.
- [30] Brown, A.C.S., Hargreaves, J.S.J., Taylor, S.H., (1999) *Catalysis Letters*, 57, 109-113.
- [31] Zhang, X., He, D.H., Zhang, Q.J., Ye, Q., Xu, B.Q. and Zhu, Q.M., (2003) *Applied Catalysis A*, 249, 107-117.
- [32] Jin, G., Lu, G., Guo, Y., Guo, Y., Wang, J. and Liu, X., (2004) *Catalysis Today*, 93-95, 173-182.
- [33] Jin, G., Lu, G., Guo, Y., Guo, Y., Wang, J., Liu, X., Kong, W. and Liu, X., (2004) *Catalysis Letters*, 97, 191-196.
- [34] Bhaskar, T., Reddy, K.R., Kumar, C.P., Murthy, M.R.V.S., Chary, K.V.R., (2001) *Applied Catalysis*, 211, 189-201.
- [35] Haber, J., Machej, T. and Grabowski, R., (1989) *Solid State Ionics*, 32-33, 887-892.
- [36] Stampfl, S.R., Chen, Y., Dumesic, J.A., Niu, Ch. and Hill, C.G., (1987) *Journal of Catalysis*, 105, 445-454.
- [37] Kaluža, L., Vít, Z. and Zdražil, M., (2005) *Applied Catalysis A*, 282, 247-253.
- [38] Kaluža, L. and Zdražil, M., (2002) *Catalysis Letters*, 78, 313-318.
- [39] Kaluža, L. and Zdražil, M., (2001) *Carbon*, 39, 2023-2034.
- [40] Gulková, D., Kaluža, L., Vít, Z. and Zdražil, M., (2006) *Catalysis Letters*, 112, 193-196.
- [41] Moya, S.A. and Escudéy, M., (1994) *Journal of the Chemical Society - Chemical Communication*, 16, 1829-1830.
- [42] Gregg, S.J. and Sing, K.S.W., *Adsorption, surface area and porosity*, 2<sup>nd</sup> edition, London Academic Press, UK (1982).
- [43] Brunelle, J.P., (1978) *Pure and Applied Chemistry*, 50, 1211-1229.
- [44] Kaluža, L. and Zdražil, M., (2007) *Applied Catalysis A*, submitted.