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Slurry Impregnation of ZrO_2 Extrudates: Controlled EggShell Distribution of MoO_3, Hydrodesulfurization Activity, Promotion by Co

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Abstract Catalysts with eggshell/uniform Mo concentration profiles were prepared by a reaction of ZrO_2 and $ZrO(OH)_2$ extrudates with an aqueous slurry of MoO_3. The thickness of the shell was regulated by the amount of MoO_3. $CoCO_3$ was adsorbed onto MoO_3/ZrO_2 from its aqueous slurry. The ZrO_2-supported catalysts were compared to their TiO_2-supported and industrial reference Al_2O_3-supported counterparts in a model reaction of benzothiophene hydrodesulfurization.

Keywords MoO_3/ZrO_2 · Eggshell Mo catalyst · $CoMo/ZrO_2$ · $CoMo/TiO_2$ · Slurry impregnation · Benzothiophene hydrodesulfurization

1 Introduction

Catalysts based on ZrO_2-supported MoO_3 exhibit many applications in reactions of industrial importance such as oxidation [1–7], hydrorefining [8–17], metathesis [18], isomerization [19], and water–gas shift [20], in which shaped forms of the catalysts are mostly used. However, the open literature, up to the authors' knowledge, focuses mostly on Mo deposition onto the support grains instead of a shaped form, like extrudates or tablets. In the field of hydrodesulfurization (HDS), only limited effort has been devoted to the impregnation of the most common support, Al_2O_3. The impregnation method using an aqueous solution of $(NH_4)_6Mo_7O_{24}$ was studied in the works [21–25]. It was found that lower pH and a higher concentration of the solution, higher temperature, and accelerated drying promoted the formation of a shallow eggshell Mo profile. We, on the other hand, have proposed a new method, called "slurry impregnation" or "water-assisted spreading", which leads to a sharp and deep Mo eggshell in the Al_2O_3 [26] or TiO_2 [27] extrudates. The method is based on the reaction of MoO_3 with the extrudates in water, and its main advantage lies in the fact that it does not produce any waste solution, only distilled water, during drying.

Techniques used in the literature [21–27] for the evaluation of Mo profiles in the extrudates or tablets include electron probe micro-analysis (EPMA) and reduction with a hydrazine–hydrochloric solution, with gaseous hydrogen or with a gaseous mixture of hydrogen and hydrogen sulfide. Quite recently, UV-vis and Raman microscopy [28–33], Tomographic Energy Dispersive Diffraction Imaging [34], and Multinuclear Magnetic Resonance Imaging [35] have been proposed as powerful tools for investigation into the preparation of Al_2O_3-supported Co-, Mo-, and P-containing hydrodesulfurization catalysts. It was corroborated that a low pH (5.0) of the impregnation solution resulted in the slow transport of Mo anions into the catalysts because of the strong interaction between these compounds and the support, whereas at high pH (9.0) the interactions were weak and the transport fast. However, at high pH, the drying (calcination) caused a reagglomeration of the poorly-bound Mo species over the external part of the extrudates. This was partially suppressed by the presence of a complexing agent such as citrates, or phosphorus in the Mo impregnation solution [28, 31]. Research [30, 33] into the deposition of Keggin-type complexes $H_xPMo_{11}CoO_{40}{}^{(7-x)-}$ has shown that a homogeneous, eggshell or eggyolk distribution of the complex may be obtained by varying the composition of the impregnation solution

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(mainly the P/Mo ratio), aging time and drying procedure. Nonetheless, any impregnated species recrystallizes if the concentration of the compound exceeds the dispersion limits of the support.

The purpose of the work being presented is to report briefly on the deposition of MoO_3 onto ZrO_2 and $ZrO(OH)_2$ extrudates and of $CoCO_3$ onto MoO_3/ZrO_2 catalysts with saturated adsorption loading of MoO_3 while applying the principles of the slurry impregnation method. Since the depositions proceed via adsorption from an aqueous slurry of extremely low-solubility precursors, it is not possible to exceed the dispersion capacity of the supports or the MoO_3/ZrO_2 catalysts. The process of Mo and Co deposition was monitored visually after reduction sulfidation in a H_2/H_2S mixture and by electron probe microanalysis. The activities of the prepared catalysts were determined in their sulfided stage in the model reaction of benzothiophene hydrodesulfurization (HDS) in a laboratory gas-phase fixed-bed reactor. Unfortunately, the internal diameter of the laboratory reactor did not enable us to evaluate the activity of catalysts in the form of extrudates thus only the extrudates with uniform and saturated profile of MoO_3 concentration were tested after crushing to the particle size fraction 0.16–0.32 mm. This approach was, nonetheless, convenient to compare the activity of the prepared ZrO_2-supported catalysts containing saturated adsorption loadings of MoO_3 and CoO with their TiO_2-supported counterparts and industrial reference Al_2O_3-supported catalysts.

2 Experimental

2.1 Supports

The ZrO_2 (AlfaAesar, Product No. 43815) extrudates were of an external diameter of 3.2 mm, an average length of 8 mm, a BET surface area of 108 m^2g^{-1}, pore volume of 0.255 cm^3g^{-1} and a BJH average pore diameter of 8.0 nm. The $ZrO(OH)_2$ (MEL Chemicals, an industrial sample) extrudates with an external diameter of 3 mm and average length of 10 mm contained approximately 15 wt.% of Al_2O_3 as a binder. Its BET surface area, pore volume and BJH average pore diameter were 311 m^2g^{-1}, 0.166 cm^3g^{-1} and 2.2 nm, respectively.

2.2 Preparation of Mo Catalysts

The MoO_3 (Fluka, Product No. 69850) was being ground in a planetary mill for 24 h before use. The mixture consisting of 15 g of support extrudates, 6.43 g of MoO_3, and 50 mL of H_2O was being heated under a reflux condenser at 95 °C, with the samples of the six extrudates removed at various time intervals, subsequently washed with water, dried in a rotary vacuum evaporator at 100 °C, sulfided in a H_2/H_2S mixture (see Sect 2.5. for the details of sulfidation), bisected and scanned. Reduction sulfidation changed the MoO_3 from light gray to black without affecting the color of the white-shadow zirconias. At the end of impregnation, the unreacted slurry of MoO_3 was separated from the remaining extrudates by decantation. The resulting saturated extrudates were dried and analyzed for MoO_3 content by atomic absorption spectroscopy (AAS) and designated $7.6MoO_3/ZrO_2$ and $20.8MoO_3/ZrO(OH)_2$, where 7.6 and 20.8 represented the determined MoO_3 content in wt.%. The $7.6MoO_3/ZrO_2$ extrudates were crushed and sieved to a grain-size fraction of 0.16-0.32 mm so that the HDS activity could be determined. The catalyst $7.6MoO_3/ZrO_2$(CIM) was prepared by the conventional impregnation method of the support grains with an aqueous solution of $(NH_4)_6Mo_7O_{24}$ (vacuum drying of an excess of the impregnation solution) as has been reported elsewhere [17].

Additionally, the $ZrO(OH)_2$ was allowed to react with the MoO_3/H_2O slurry at 25 and 95 °C. Three loadings of MoO_3, namely 5, 10, and 15 wt.% (calculated per solid part of the mixtures), were used. At the end of the slurry impregnation, all the MoO_3 disappeared from the mixtures and the extrudates were dried in a vacuum evaporator at 100 °C. The actual content of MoO_3 in the final catalysts was analyzed by AAS and was proved to be the same as the nominal one.

The TiO_2-supported samples $10.5MoO_3/TiO_2$ and $10.5MoO_3/TiO_2$ (CIM) were prepared by slurry impregnation method (spreading of MoO_3 onto TiO_2 in water) and conventional impregnation method (vacuum drying of TiO_2 with an excess of an aqueous solution of $(NH_4)_6Mo_7O_{24}$), respectively. Further details about the synthesis can be found in our earlier work [27].

2.3 Preparation of CoMo Catalysts

The mixture of 5 g of $MoO_3/ZrO(OH)_2$ extrudates, 0.33 g of $CoCO_3$ (Aldrich, Product No. 202193, ground in a planetary mill for 24 h) and 18 mL of water was being heated at 95 °C. Samples of extrudates were taken at various time intervals. They were washed with water, dried in a rotary vacuum evaporator at 100 °C, bisected and analyzed with EPMA.

The catalysts $7.6MoO_3/ZrO_2$ and $10.5MoO_3/TiO_2$ in the form of the grain were saturated with Co by their being heated with an aqueous slurry of $CoCO_3$ under a reflux condenser at 95 °C for 12 h. The nominal loading of Co used for the slurry impregnation corresponded to 5 wt.% of CoO in the final catalysts. The unreacted slurry of $CoCO_3$ was removed from the grains at the end of impregnation by washing with water. The actual loading of CoO in wt.% was determined by AAS and the catalysts were labeled: $1.7CoO6.4MoO_3/ZrO_2$ and $2.6CoO10.0MoO_3/TiO_2$.

Co was also deposited over the $7.6MoO_3/ZrO_2$ and $10.5MoO_3/TiO_2$ catalysts grains by the conventional impregnation method from an aqueous solution of $Co(NO_3)_2$ (vacuum drying of an excess of the aqueous impregnation solution) and by impregnation of a pre-sulfided form of those catalysts from a methanolic solution of cobalt–acetylacetonate, $Co(C_5H_7O_2)_2$, (vacuum drying of an excess of the methanolic impregnation solution). The catalysts were designated as follows: $2.4CoO(CIM)11.5MoO_3/TiO_2$ and $3.2CoO(MIM)11.1MoS_2/TiO_2$, where CIM and MIM were used to refer to the Co deposited by the conventional aqueous impregnation method and methanolic impregnation method, respectively. The method of pre-sulfidation is described in Sect 2.5 below.

2.4 Characterization of the Materials

The point of zero charge (PZC) was measured by means of a simplified mass titration method [36] with a WTW pH meter equipped with a cell Hamilton Slimtrode. The PZC of the selected samples was also obtained from a plot of zeta potential versus pH, an example of which is given in Fig. 1. The zeta potential was measured with a Coulter Delsa 440 SX (Coulter Electronic, USA). Prior to the measurement, the pH of each sample (0.04 g of solid sample and 40 mL of water) was adjusted with NaOH or HCl.

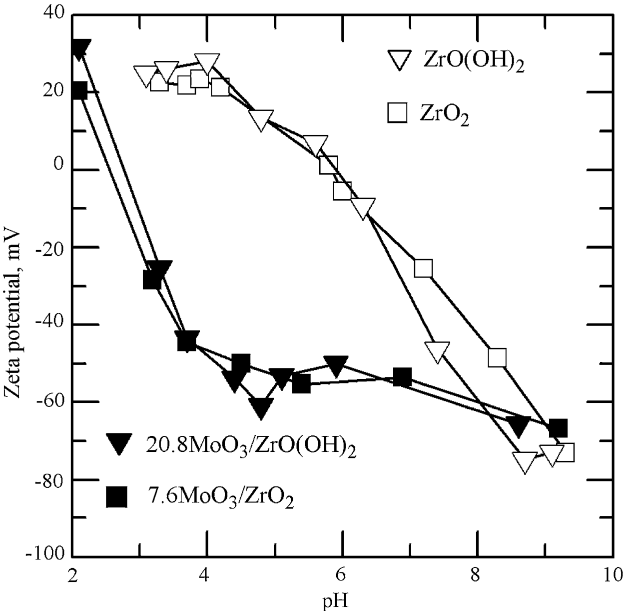

Fig. 1 Examples of the dependence of the zeta potential on the pH determined over the zirconias and the catalysts with saturated adsorption loading of MoO_3

The specific surface area was determined by the common Brunauer, Emmett, and Teller (BET) procedure using a Micromeritics ASAP 2010M instrument after evacuating of the samples at 350 °C for 4 h. The average pore diameter was acquired from the desorption branch of the adsorption-desorption isotherms by the Barrett-Joyner-Halenda (BJH) method.

The Co and Mo content in the saturated catalysts were analyzed by atomic adsorption spectroscopy (AAS) with GBC Avanta instrument. Bisected catalyst extrudates were analyzed using electron probe micro-analysis (EPMA). A JEOL JXA electron microscope was equipped with the ED analyzer EDAX PV 9400. Each point of Co loading represents an average recorded and calculated over the area 60×60 μm at a given distance from the extrudates' centers.

2.5 Benzothiophene Hydrodesulfurization

Benzothiophene (BT) hydrodesulfurization (HDS) was carried out in the gas-phase in a fixed-bed tubular-flow microreactor (i.d. 3 mm). The catalysts were presulfided in a H_2S/H_2 flow (1/10) at a temperature ramp 10 °C min^{-1} to 400 °C and a dwell time of 1 h. The composition of the starting reaction mixture was kept constant; namely, the mixture contained 16,200 and 1,384 kPa of BT, decane and hydrogen, respectively. The catalyst charge (W) was varied from 0.02 to 0.4 g, depending on its activity, and was diluted with inert α-Al_2O_3 to form a bed of a length of 30 mm. The particle size fraction 0.16–0.32 mm of the catalysts and α-Al_2O_3 diluent was used for the experiments. Over the reference CoMo catalyst KF, it was checked that this particle size fractions exhibited the same activity as lower fraction 0.08–0.16 mm so the influence of internal diffusion was eliminated. The reaction was run at 360 °C and at three feed rates of BT: 7.7, 10.3 and 15.5 mmolh^{-1}. The steady state was reached 20 min after each feed-rate change, with no deactivation of the catalysts observed. The reaction mixture was analyzed on a Hewlett-Packard gas chromatograph (6890 series) equipped with a capillary column HP-5 (30 m, 0.53 mm, 1.5 μm) and flame ionization detector. The reaction products were dihydrobenzothiophene (DHBT) and ethylbenzene (EB). The following parameters were determined: (i) the relative composition of the reaction mixture, a_i, ($a_{BT} = n_{BT}/n^o_{BT}$, $a_{DHBT} = n_{DHBT}/n^o_{BT}$, $a_{EB} = n_{EB}/n^o_{BT}$, where n^o and n were the initial and final numbers of the moles, respectively); (ii) the empiric rate constant of ethylbenzene formation k_{EB}, which was acquired by a non-linear fitting of the dependence a_{EB} on W/F_{BT} using the equation $a_{EB} = 1 - \exp(-k_{EB}\ W/F_{BT})$; and (iii) a selectivity index a_{EB}/a_{DHBT} at $a_{BT} = 0.5$, which was taken from a graph of the fitting of the dependence of a_{BT}, a_{EB} and a_{DHBT} on W/F_{BT} by four pseudo-first-order constant reaction schemes (BT to DHBT, DHBT to BT, DHBT to EB, and BT to EB).

The activity k_{EB} and selectivity a_{EB}/a_{DHBT} of the prepared catalysts were compared with those of the $15MoO_3/Al_2O_3$ (BASF M 8–30, Germany, 210 m^2g^{-1}) and $3.2CoO15.5MoO_3/Al_2O_3$ (Albemarle KF 756, the Netherlands, 264 m^2g^{-1}) industrial samples.

2.6 Packing Density

For the purpose of comparing the activity normalized per unit volume, the packing density of the supports and industrial catalysts in the form of the grain was determined on an analytical balance in a 5 mL cylinder after dabbing off five times.

3 Results and Discussion

3.1 Slurry Impregnation of Zirconias

It was found that the point of zero charge determined by the simplified mass titration method of ZrO_2 and $ZrO(OH)_2$ was 7.3 and 8.0, respectively, which was systematically higher than the value of 6.0 taken from the graph of zeta potentials in Fig. 1. Nevertheless, all those PZCs were significantly higher than the pH 2.1 of the MoO_3 impregnation slurry. The surfaces of the zirconias were therefore positively charged, which made the adsorption of the dissolved anionic Mo species possible. Since the adsorption of Mo was strong under that condition, radial Mo eggshell concentration profiles were formed. The gradual adsorption of Mo species was observed visually after sulfidation as shown in Fig. 2. Unfortunately, the signals of Zr and Mo partially overlapped in the electron probe microanalysis, thus precluding the quantification of the Mo content in the eggshells. Nevertheless, we found earlier [26] that the determination of the thickness of the eggshell by the sulfidation method is in good agreement with the EPMA method. Furthermore, the uniformly-saturated extrudates with MoO_3 were analyzed by AAS. It was found that the ZrO_2 and $ZrO(OH)_2$ saturated with MoO_3 contained 3.3 and 3.5 atoms Mo per nm^2 after 75 and 11 h of impregnation, respectively.

The correlations between (i) the saturated adsorption loadings of MoO_3 achieved over the zirconias studied and those achieved before over Al_2O_3 [26] and TiO_2 [27], (ii) the specific surface area of those supports, and (iii) the time needed for the saturation of the supports are plotted in Fig. 3. It was found that the saturated loadings were tightly and linearly proportional to the surface areas, whereas the time needed for the saturation of the carriers was inversely proportional to the specific areas. The latter correlation should be considered only qualitatively, because the rate of impregnation is also affected by other parameters than the surface area, e.g., by the diameter of the particles, the particle geometry and nominal loading of MoO_3 used for impregnation.

The impregnation of $20.8MoO_3/ZrO(OH)_2$ extrudates from the $CoCO_3/H_2O$ slurry was monitored by EPMA (see Fig. 4 for the results). It was found that Co was being adsorbed in the form of eggshell profiles from the beginning of impregnation and an almost uniform concentration profile was achieved after 78 h. The impregnation of $7.6MoO_3/ZrO_2$ extrudates by the $CoCO_3/H_2O$ slurry was not performed for two reasons: (i) we had found earlier [37] for Al_2O_3 of the surface area 282 m^2g^{-1} that the deposition from the slurry was about 20-fold slower in the case of $CoCO_3$ than in the case of MoO_3 and (ii) the saturation of the ZrO_2 extrudates with MoO_3 had already took

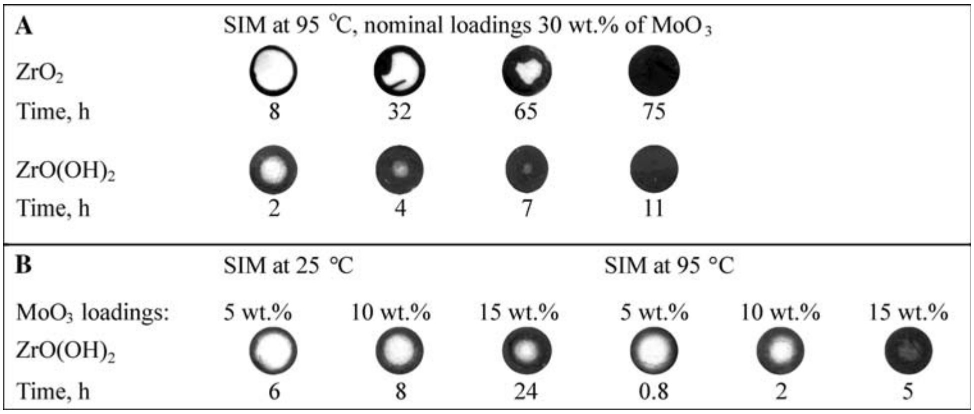

Fig. 2 Mo eggshells obtained by the slurry impregnation method (SIM) over ZrO_2 and $ZrO(OH)_2$ extrudates of an e.d. of 3.0 and 3.2 mm, respectively. **a** slurry impregnation with the nominal loading of MoO_3 being higher than the saturated adsorption loading; the unreacted slurry of MoO_3 was removed by washing in water at the time given. **b** slurry impregnation with nominal loading being lower than the saturated adsorption loading; all MoO_3 had been adsorbed at the time given. Black—MoS_2, white-shadow—unloaded supports

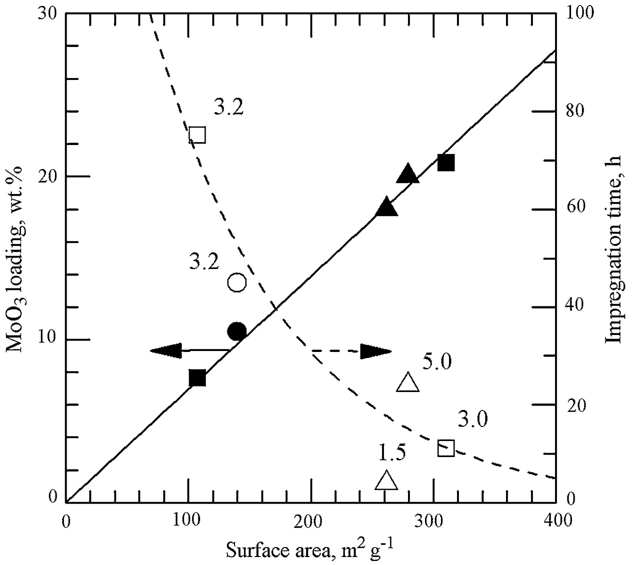

Fig. 3 The dependence of saturated adsorption loadings of MoO_3 (solid line and filled symbols) and impregnation time needed for the saturation (dashed line and open symbols) on the surface areas S_{BET} of the supports: squares—ZrO_2 and $ZrO(OH)_2$, circles—TiO_2 [27], and triangles— Al_2O_3 [26]. The numbers denote the external diameters in mm of the extrudates or balls studied

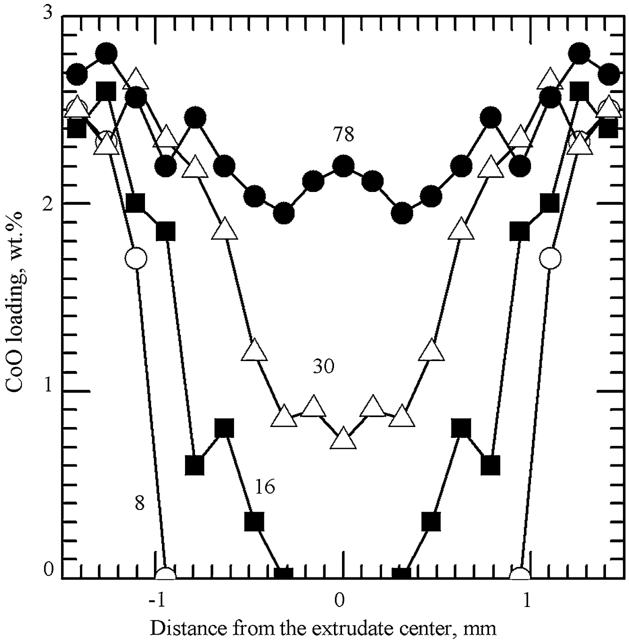

Fig. 4 CoO concentration profiles evaluated by electron probe microanalysis in CoMo/ZrO(OH)$_2$ extrudates prepared by impregnation of 20.8MoO$_3$/ZrO(OH)$_2$ from an aqueous slurry of $CoCO_3$ at 95 °C. The numbers denote impregnation times in hours

75 h because of its low surface area (see Fig. 3). The slurry impregnation of 7.6MoO$_3$/ZrO$_2$ with $CoCO_3$ would thus take impractically long.

Due to the long time needed to saturate the extrudates, the 7.6MoO$_3$/ZrO$_2$ catalyst and its TiO_2-supported counterpart were impregnated only in the form of grains. The adsorption loadings achieved after a 12-h reaction are included in the name of the catalysts in wt.% of CoO and are summarized in Table 1 and 2.

Despite the extremely low solubility of $CoCO_3$ in water, namely ca 0.0001 g per 100 mL at 25 °C [38], and the rather slow adsorption, the experiments clearly showed the feasibility of the slurry impregnation method application for the deposition of the compound onto supports loaded with a saturated MoO_3 adsorption monolayer, which could be explained by the low PZCs of the catalysts containing a saturated MoO_3 monolayer. The PZCs of 7.6MoO$_3$/ZrO$_2$, 20.8MoO$_3$/ZrO(OH)$_2$ and 10.5MoO$_3$/TiO$_2$ were found to be 2.4, 2.6 and 2.3, respectively (determined by the simplified mass titration method), and 2.5, 2.8, and 2.0, respectively (taken from Fig. 1). These values do not differ much from the value 2.1 (determined by the simplified mass titration method) of pure MoO_3, and thus the surfaces of the prepared catalysts could be assumed to have been mostly covered by MoO_3. This has alrady been assumed in the literature about monolayer MoO_3/Al_2O_3 [39], WO_3/Al_2O_3 [40], or V_2O_5/Al_2O_3 [41] catalysts for example. The surfaces of the prepared MoO_3 monolayer catalysts were therefore negatively charged and the adsorption of dissolved Co cations from the slightly basic $CoCO_3/H_2O$ slurry of pH 8.6 was favored.

To conclude, the depth of Mo (Co) eggshell can be easily regulated in two ways: either by the spreading time or by the nominal amount of MoO_3 ($CoCO_3$). Bearing in mind the practical implications, the latter is the method of choice. To demonstrate its feasibility, the selected nominal loadings of MoO_3 were used to saturate ZrO(OH)$_2$ (see Fig. 2). All the MoO_3 had been adsorbed at the time given, and distinct eggshells were formed. All solid MoO_3 had disappeared from the slurry at the end of impregnation. In principle, the only by-product of the slurry impregnation method is distilled water because the low amount of dissolved Mo species that are present in mother liquor is deposited onto a surface during the drying process. As calcination is not needed, the catalyst may be directly inserted into a hydrodesulfurization reactor.

3.2 Hydrodesulfurization Activity

The activities of the prepared and industrial catalysts were evaluated on the model reaction of benzothiophene hydrodesulfurization and expressed as empiric pseudo-first-order rate constants of the ethylbenzene formation k_{EB}. The examples of how they were obtained are shown in Fig. 5. The particle size fraction (0.16–0.32 mm) of the catalysts with uniform and saturated loadings was used for the activity measurements because the laboratory apparatus enabled to test catalysts only in the form of grain. The

Table 1 Activity of the prepared and reference catalysts in the HDS of benzothiophene

Catalysts	HDS activity normalized per					
	Mol of Mo (Co + Mo)		Catalyst weight		Catalyst volume	
	k_{EB}, mol_{EB} $mol^{-1}h^{-1}$	A_R[a]	k_{EB}, $mmol_{EB}$ $g^{-1}h^{-1}$	A_R[a]	k_{EB}, $mmol_{EB}$ $cm^{-3}h^{-1}$	A_R[a]
Mo catalysts						
$7.6MoO_3/ZrO_2$	58	2.1	30	1.0	37	2.2
$7.6MoO_3/ZrO_2$ (CIM)	51	1.9	27	0.9	33	1.9
$10.5MoO_3/TiO_2$	54	2.0	40	1.4	35	2.0
$10.5MoO_3/TiO_2$ (CIM)	53	2.0	39	1.3	34	2.0
$15MoO_3/Al_2O_3$ (BASF)	27	1.0	29	1.0	17	1.0
CoMo catalysts						
$1.7CoO6.4MoO_3/ZrO_2$	182	0.6	122	0.3	149	0.5
$2.0CoO(CIM)7.4MoO_3/ZrO_2$	107	0.4	96	0.2	121	0.4
$1.7CoO(MIM)8.2MoS_2/ZrO_2$	250	0.9	188	0.4	238	0.8
$2.6CoO10.0MoO_3/TiO_2$	157	0.6	163	0.4	147	0.5
$2.4CoO(CIM)11.5MoO_3/TiO_2$	142	0.5	159	0.4	146	0.5
$3.2CoO(MIM)11.1MoS_2/TiO_2$	176	0.6	197	0.5	181	0.6
$3.2CoO15.5MoO_3/Al_2O_3$ (KF)	282	1.0	421	1.0	300	1.0

[a] A_R—relative activity

Table 2 Promotional effect of Co on the HDS activity of the Mo catalysts prepared

Catalyst	Molar ratio	Promotional effect of Co ($k_{EB}^{CoMo}/k_{EB}^{Mo}$) normalized per		
	(Co/Co + Mo)	Mol of Co + Mo	Catalyst weight	Catalyst volume
$1.7CoO6.4MoO_3/ZrO_2$	0.34	3.1	4.1	4.0
$2.0CoO(CIM)7.4MoO_3/ZrO_2$	0.29	1.8	3.2	3.3
$1.7CoO(MIM)8.2MoS_2/ZrO_2$	0.31	4.3	6.3	6.4
$2.6CoO10.0MoO_3/TiO_2$	0.33	2.9	4.1	4.2
$2.4CoO(CIM)11.5MoO_3/TiO_2$	0.29	2.6	4.0	4.2
$3.2CoO(MIM)11.1MoS_2/TiO_2$	0.38	3.3	4.9	5.2

activities were normalized per number of mol of the active metals or per unit weight or volume of the catalyst. The normalization per mol of the active metals makes it possible to compare the activities of the catalysts with different loadings (as it was shown in Fig. 3, the saturated adsorption loadings depended on the surface areas of the ZrO_2 and TiO_2 supports). This activity is an intrinsic property of the sulfided transition metal and its interaction with the support. On the contrary, the activity normalized per unit weight or volume represent and an integral value of HDS activity. The normalization per unit volume was calculated using the determined packing density of 1.14, 0.79, 0.60 and 0.71 gcm^{-3} of the ZrO_2, TiO_2, Mo/Al_2O_3 BASF and $CoMo/Al_2O_3$ KF 756, respectively. The volume based activity provides a basis of comparison for commercial HDS processes as the reactor volume is generally fixed in existing facilities. For the sake of clarity, the relative activities of the prepared catalysts A_R were calculated as the ratio of the k_{EB} of the prepared catalyst to the k_{EB} of the industrial reference counterpart. An overview of the HDS activities is shown in Table 1, which, however, does not contain data on the $ZrO(OH)_2$-supported catalysts, because we have previously found that they exhibited extremely low HDS activity, (see [17] for further details).

It was ascertained that the intrinsic activity of the Mo deposited by the slurry impregnation method was slightly higher than the activity of the Mo deposited by conventional impregnation from an aqueous $(NH_4)_6Mo_7O_{24}$ solution. The Mo deposited over ZrO_2 and TiO_2 was, moreover, approximately twice as active as the Mo deposited over Al_2O_3 in the industrial reference catalyst. After normalization, the ZrO_2- and TiO_2-supported Mo catalysts retained their high activity per unit volume while losing their advantage per unit weight due to the relatively higher packing density of ZrO_2 and TiO_2 to the Mo/Al_2O_3.

Furthermore, the impregnation method using the $CoCO_3/H_2O$ slurry was found to be efficient for the enhancement of the HDS activity of the ZrO_2- and TiO_2-

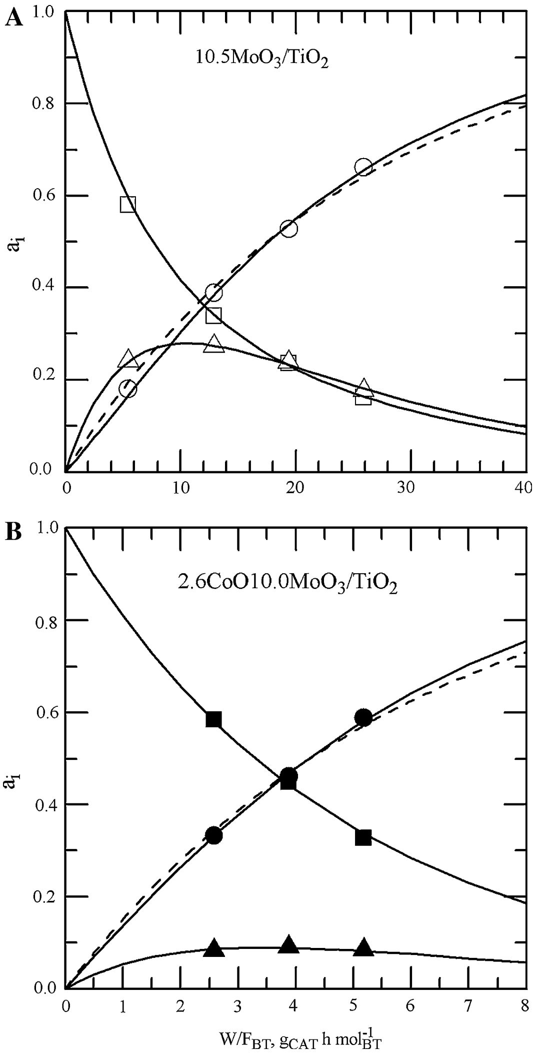

Fig. 5 Examples of the kinetic curves of benzothiophene HDS. Squares—benzothiophene, triangles—dihydrobenzothiophene, and circles—ethylbenzene. The solid and dashed curves have been calculated using the four pseudo-first-order reaction schemes and the empiric psedo-first-order equation of ethylbenzene formation, respectively

supported MoO_3 catalysts. The promotional effect of Co on HDS activity was quantified as a ratio of the formal-rate constant determined over a CoMo catalyst to the formal-rate constant determined over a corresponding Mo counterpart ($k_{EB}^{CoMo}/k_{EB}^{Mo}$). The promotional effects are summarized in Table 2.

It was ascertained that the methods of Co deposition over ZrO_2- and TiO_2-supported MoO_3 catalysts may be ordered on the basis of the resulting HDS activity and the promotional effects as follows: the conventional deposition from an aqueous $Co(NO_3)_2$ solution < the slurry impregnation with $CoCO_3$ < the deposition from a methanolic $Co(C_5H_7O_2)_2$ solution onto a pre-sulfided Mo catalyst.

As the promotional effect of Co on the activity in the HDS of benzothiophene was observed to be accompanied by a relative increase of C–S hydrogenolysis (HYG) to C=C hydrogenation (HYD), which was manifested by a decrease of the formation of hydrogenation intermediate dihydrobenzothiophene, a selectivity index a_{EB}/a_{DHBT} was calculated as a ratio of the relative composition of ethylbenzene to the relative composition of dihydrobenzothiophene at the relative composition of benzothiophene 0.5. The promotional effect and selectivity index were plotted against the HDS activity in Fig. 6. First, it was found that the a_{EB}/a_{DHBT} selectivity increased roughly linearly with the increasing HDS activity. Second, the ZrO_2 and TiO_2 supports hardly influenced the relative selectivity a_{EB}/a_{DHBT} of the deposited Mo while the intrinsic HDS activity of that Mo was two times higher than was achieved over the reference Al_2O_3-supported Mo catalyst. The CoMo catalysts supported over ZrO_2 and TiO_2 supports, however, exhibited lower a_{EB}/a_{DHBT} selectivities and HDS activities than the reference catalyst CoMo supported over Al_2O_3. The effect of the ZrO_2 and TiO_2 supports may therefore be considered as detrimental to the activity of the bimetallic CoMo phase. The most promising method of Co deposition, the promotion of the presulfided Mo by cobalt–acetylacetonate, only partially compensated for this disadvantage. These results are in good agreement with previous literature data [16, 42]. For example, the

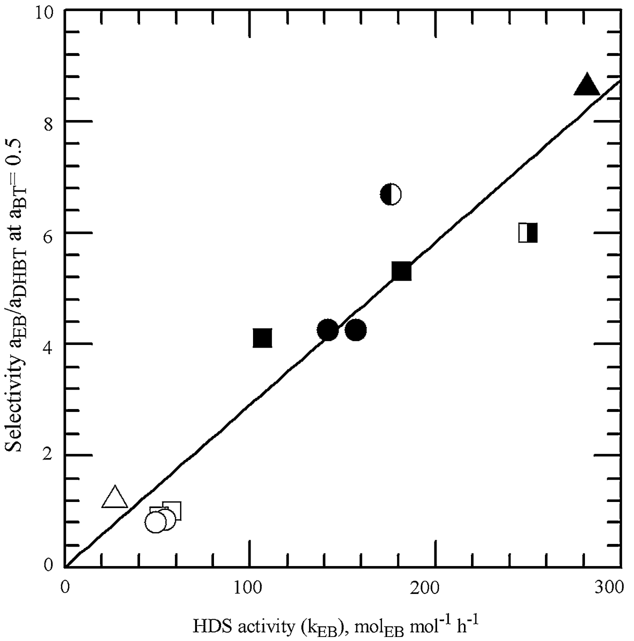

Fig. 6 The dependence of the selectivity index on HDS activity over the prepared and reference catalysts. The squares, circles and triangles were used for the ZrO_2-, TiO_2- and reference industrial Al_2O_3-suported catalysts, respectively. Open symbols—Mo catalysts, filled symbols—CoMo catalysts with Co deposited by SIM or CIM, half-filled symbols—CoMo catalysts with Co deposited by MIM over presulfided Mo catalysts

promotional effects of 2.4 and 2.9 in the case of Co over zirconia- and titania-supported catalysts, respectively, in [42] or 3.3 over both supports in [16] were reported while they were about 5 or 11 over alumina-supported counterparts resulting in high integral HDS activity. On contrary, it is believed that further improvement of the ZrO_2 and TiO_2 based catalysts lie in tailored preparation of their mixed form with desirable textural properties [43–45] or nanostructured forms [46, 47]. The CoMo catalyst supported on solvo-thermally treated ZrO_2–TiO_2 with molar ratio ZrO_2/TiO_2 30/70 and BET surface area 313 m^2g^{-1} exhibited promotional effect about 3.2 but exceeded the HDS activity of a reference Al_2O_3-supported counterpart about twofold [43]. The promotional effect of 8.5 was reached after deposition of Co onto presulfided Mo catalysts supported on ZrO_2–TiO_2 with molar ratio ZrO_2/TiO_2 60/40 and BET surface area 165 m^2g^{-1}, which resulted in 10% activity improvement in comparison with Al_2O_3 supported catalyst [44]. Two fold higher HDS activities of CoMo catalysts were reported over nano-structured TiO_2 possessing BET surface area about 330 m^2g^{-1} [46] and TiO_2 nanotubes of BET surface area 236 m^2g^{-1} [47] than over Al_2O_3-supported counterparts but without referring on promotional effects. A relatively high promotional effect of 10 was obtained in the case of Ni supported over wide-pore ZrO_2–TiO_2 Mo catalyst (molar ratio ZrO_2/TiO_2 30/70 and BET surface area about 300 m^2g^{-1}) employing chelating agent assisted impregnation technique [45]. It could be assumed that applying the same preparation technique to the ZrO_2 support studied within the present work could led to further improvement of the HDS activity.

4 Conclusions

It has been shown that the slurry impregnation method is suitable for the deposition of MoO_3 onto the extrudates of ZrO_2 and $ZrO(OH)_2$ in order to form an eggshell radial profile of Mo concentration. This method, moreover, does not make it possible to exceed the dispersion capacity of the support surface. The thickness of the eggshell can be efficiently regulated by the amount of MoO_3 used. Co can be deposited over the ZrO_2- and TiO_2-supported catalysts containing a saturated adsorption monolayer of MoO_3 from an aqueous slurry of low solubility $CoCO_3$. The slurry impregnation method is a clean and simple method of Co and Mo deposition, which does not introduce any ions like $NH_4^{(+)}$ or $NO_3^{(-)}$; furthermore, calcination is not needed, and only water is produced during drying. The activity of the Mo supported on ZrO_2 and TiO_2 in the hydrodesulfurization of benzothiophene was about twice as high as the activity of the Mo in the industrial Al_2O_3-supported catalyst. The activity of CoMo ZrO_2- and TiO_2-supported catalysts, however, was not as high as the activity of the industrial, Al_2O_3-supported counterpart.

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References

1. Brown ACS, Hargreaves JSJ, Taylor SH (1999) Catal Lett 57:109
2. Zhang X, He DH, Zhang QJ, Ye Q, Xu BQ, Zhu QM (2003) Appl Catal A 249:107
3. Kim DS, Wachs IE, Segawa K (1994) J Catal 146:268
4. Jin G, Lu G, Guo Y, Guo Y, Wang J, Liu X (2004) Catal Today 93–95:173
5. Jin G, Lu G, Guo Y, Guo Y, Wang J, Liu X, Kong W, Liu X (2004) Catal Lett 97:191
6. Chary KVR, Reddy KR, Kishan G, Niemantsverdriet JW, Mestl G (2004) J Catal 226:283
7. Bhaskar T, Reddy KR, Kumar CP, Murthy MRVS, Chary KVR (2001) Appl Catal 211:189
8. Duchet JC, Tilliette MJ, Cornet D, Vivier L, Perot G, Bekakra L, Moreau C, Szabo G (1991) Catal Today 10:579
9. Weissman JG, Ko EI, Kaytal S (1993) Appl Catal A 94:45
10. Vrinat M, Hamon D, Breysse M, Durand B, des Courieres T (1994) Catal Today 20:273
11. Afanasiev P, Geantet C, Breysse M (1995) J Catal 153:17
12. Orozco EO, Vrinat M (1998) Appl Catal 170:195
13. Pizzio L, Vázquez P, Cáceres C, Blanco M (1999) Stud Surf Sci Catal 127:413
14. Maity SK, Rana MS, Srinivas BN, Bej SK, Murali Dhar G, Prasada Rao TSR (2000) J Mol Catal 153:121
15. Breysse M, Afanasiev P, Geantet C, Vrinat M (2003) Catal Today 86:5
16. Ji Y, Afanasiev P, Vrinat M, Li Wenzhao, Li Can (2004) Appl Catal A 257:157
17. Kaluža L, Zdražil M (2007) Appl Catal A 329:58
18. Indovina V, Cimino A, Cordischi D, Della Bella S, De Rossi S, Ferraris G, Gazzoli D, Occhiuzzi M, Valigi M (1993) Stud Surf Sci Catal 75:875
19. Yori JC, Pieck CL, Parera JM (2000) Catal Lett 64:141
20. Łaniecki M, Małecka-Grycz M, Domka F (2000) Appl Catal A 196:293
21. Srinivasan R, Liu HC, Wehler SW (1979) J Catal 57:87
22. Goula MA, Kordulis C, Lycourghiotis A (1992) J Catal 133:486
23. Goula MA, Kordulis C, Lycourghiotis A, Fierro JLG (1992) J Catal 137:285
24. Hanika J, Janoušek V, Sporka K (1987) Collect Czech Chem Commun 52:663
25. Okamoto Y, Umeno S, Arima Y, Nakai K, Takahashi T, Uchikawa K, Inamura K, Akai Y, Chiyoda O, Katada N, Shishido T, Hattori H, Hasegawa S, Yoshida H, Segawa K, Koizumi N, Yamada M, Nishijima A, Kabe T, Ishihara A, Isoda T, Mochida I, Matsumoto H, Niwa M, Uchijima T (1998) Appl Catal A 170:343
26. Kaluža L, Zdražil M (2002) Catal Lett 78:313
27. Gulková D, Kaluža L, Vít Z, Zdražil M (2006) Catal Lett 112:193
28. Bergwerff JA, Visser T, Leliveld BRG, Rossenaar BD, de Jong KP, Weckhuysen BM (2004) J Am Chem Soc 126:14548
29. van de Water LGA, Bergwerff JA, Niijhuis TA, de Jong KP, Weckuysen BM (2005) J Am Chem Soc 127:5024

30. van de Water LGA, Bergwerff JA, Leliveld BRG, Weckhuysen BM, de Jong KP (2005) J Phys Chem B 109:14513
31. Bergwerff JA, Jansen M, Leliveld BRG, Visser T, de Jong KP, Weckhuysen BM (2006) J Catal 243:292
32. Bergwerff JA, Visser T, Weckhuysen BM (2008) Catal Today 130:117
33. Bergwerff JA, van de Water LGA, Visser T, de Peinder P, Leliveld BRG, de Jong KP, Weckhuysen BM (2005) Chem Eur J 11:4591
34. Beale AM, Jacques SDM, Bergwerff JA, Barnes P, Weckhuysen BM (2007) Angew Chem Int Ed 46:8832
35. Lysova AA, Koptyug IV, Sagdeev RZ, Parmon VN, Bergwerff JA, Weckhuysen BM (2005) J Am Chem Soc 127:11916
36. Moya SA, Escudey M (1994) J Chem Soc, Chem Commun 16:1829
37. Kaluža L, Zdražil M (2007) Top Catal 45:191
38. Speight JG (2005) Lange's handbook of chemistry. McGraw Hill, New York
39. Gil Llambías FJ, Escudey Castro AM (1982) J Chem Soc Chem Commun (9):478
40. Gil Llambías FJ, Escalona N, Pfaff C, Scott C, Goldwasser J (1999) React Kinet Catal Lett 66:225
41. Gil Llambías FJ, Escudey AM, Fierro JLG, López Agudo A (1985) J Catal 95:520
42. Okamoto Y, Ochiai K, Kawano M, Kobayashi K, Kubota T (2002) Appl Catal A 226:115
43. Escobar J, Barrera MC, de los Reyes JA, Cortés MA, Santes V, Gómez E, Pacheco JG (2008) Catal Today 133–135:282
44. Afanasiev P (2008) Catal Commun 9:734
45. Escobar J, Barrera MC, de los Reyes JA, Toledo JA, Santes V, Colín JA (2008) J Mol Catal A 287:32
46. Escobar J, Toledo JA, Cortés MA, Mosqueira ML, Pérez V, Ferrat G, López-Salinas E, Torres-García E (2005) Catal Today 106:222
47. Cortés-Jácome MA, Escobar J, Angeles Chávez C, López-Salinas E, Romero E, Ferrat G, Toledo-Antonio JA (2008) Catal Today 130:56