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Synthesis of a high surface area monolayer MoO_3/MgO catalyst in a $(NH_4)_6Mo_7O_{24}$/MgO/methanol slurry, and its hydrodesulfurization activity

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High surface area MoO_3/MgO catalysts (200–270 $m^2 g^{-1}$) have been prepared by the reaction of MgO with the impregnation slurry $(NH_4)_6Mo_7O_{24}$/methanol. Molybdena was deposited and NH_3 was evolved. The texture of water sensitive MgO was stable in the slurry. The impregnation reaction was limited to the MgO surface at 25 °C where each Mo atom occupied about 0.24–0.28 nm^2 at saturation. However, impregnation probably continued into subsurface layers of MgO at 65 °C where the saturation loading corresponded to 0.13–0.16 nm^2 per Mo atom. Gradual penetration of molybdena into MgO extrudates indicated that the surface reaction between dissolved $(NH_4)_6Mo_7O_{24}$ and MgO was fast and the rate determining step of impregnation was dissolution or diffusion of $(NH_4)_6Mo_7O_{24}$. The MoO_3/MgO catalysts were prepared using various particle sizes of MgO, various loadings of MoO_3, different temperatures and impregnation times. The activity of the best MoO_3/MgO catalysts in the hydrodesulfurization of benzothiophene was similar to the activity of the commercial conventional hydrodesulfurization catalyst MoO_3/Al_2O_3.

Introduction

The system MoO_3/MgO is a catalyst or catalyst precursor in a number of industrially relevant reactions such as oxidation of hydrocarbons,[1,2] methathesis of olefins[3] and hydrodesulfurization.[4–6] Its structure has also been analysed without testing its catalytic properties, see *e.g.* refs. 7–10. The common preparation method reported in the literature is conventional impregnation of MgO by an aqueous solution of $(NH_4)_6Mo_7O_{24}$. However, MgO is chemically and texturally quite unstable in aqueous solutions and we have suggested non-aqueous impregnation to overcome this complication.[11,12]

The present work is related to hydrodesulfurization, HDS. MgO might be an interesting support for Mo sulfide based catalysts, as an alternative to the conventional Al_2O_3 support, for two main reasons. A basic support should be favourable for the formation of a perfect surface monolayer of acidic MoO_3 and should inhibit coking which occurs over relatively acidic Al_2O_3 supported catalysts. However, previous authors reported that the HDS activity of MoO_3/MgO catalysts was lower than that of its Al_2O_3 supported counterparts.[4–6] We have concluded that the reason for this was the improper application of conventional aqueous impregnation to the water sensitive MgO support.[11,12]

We have described the preparation of MoO_3/MgO catalyst by the reaction of high surface area MgO particles (0.16–0.32 mm, 250–300 $m^2 g^{-1}$) with the slurry $(NH_4)_6Mo_7O_{24}$/methanol or ethanol at the alcohol boiling point. The low solubility of $(NH_4)_6Mo_7O_{24}$ was sufficient for its gradual transport into the MgO pores where the impregnation reaction took place: molybdena was deposited and NH_3 was evolved. The evolution of NH_3 followed an approximately first order rate equation. The texture of MgO was stable in the impregnation slurry. The benzothiophene HDS activity of the best MoO_3/MgO samples prepared was similar to the activity of the industrial MoO_3/Al_2O_3 catalyst. The method was named "slurry impregnation".[11]

The following points not studied in the previous paper[11] were the subject of the present work. (i) Deposition of molybdena was achieved not only at the boiling point of methanol but also at room temperature. (ii) The method was applied to larger support particles in the form of 2.6 mm extrudates. (iii) Impregnation in the kneaded paste MgO/$(NH_4)_6Mo_7O_{24}$/methanol was tested. (iv) Information on the rate determining step of the impregnation sequence (dissolution of $(NH_4)_6Mo_7O_{24}$/diffusion into MgO pores/reaction with the MgO surface) was obtained by the measurement of the gradual penetration of Mo into extrudates. (v) The maximum (saturated) loading of molybdena that can be deposited by slurry impregnation was determined.

Experimental

MgO support

Two forms of high surface area MgO were prepared from commercial low surface area MgO (Labora, Czech Republic, grade "light", 70 $m^2 g^{-1}$). Particles (0.16–0.32 mm) were obtained by the hydration–dehydration treatment[13] as described in detail in the previous paper.[11] Extrudates were obtained by calcination of the extruded MgO/water paste (ramp 90 °C h^{-1} to 390 °C, dwell 1.5 h at 390 °C). The paste was kneaded in an electric motor driven agate mortar (the mortar is described in ref. 14) for 15 min before extrusion and it was dried at room temperature for 10 days before calcination. This procedure is important for complete hydration of the material and for good mechanical strength of the extrudates. All supports were calcined once more immediately before use with the temperature program: 25 min to 390 °C, 60 min at 390 °C. All calcinations were performed in a tubular flow reactor in an air stream: this is important for the effective removal of the evolved water.

MoO_3/MgO catalysts

Commercial $(NH_4)_6Mo_7O_{24}$ was ground in an agate mortar before use. The water content in methanol was 0.13 wt.%.

The impregnation slurry $(NH_4)_6Mo_7O_{24}$ was added to the

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support (for the amount of methanol and the impregnation temperature see below). The term "impregnation" used henceforward means in fact the chemical reaction between dissolved $(NH_4)_6Mo_7O_{24}$ and solid MgO with evolution of NH_3. The end of impregnation was qualitatively evaluated according to the decreasing amount of fine powder of $(NH_4)_6Mo_7O_{24}$ and according to the absence of NH_3 in the gas phase above the slurry as indicated by water wetted litmus paper. After impregnation, the impregnated support (particles 0.16–0.32 mm or extrudates 2.6 mm) was separated from the sludge of fine particles (mechanically and chemically eroded support and unreacted $(NH_4)_6Mo_7O_{24}$) by repeated decantation with methanol recycling. Unless otherwise stated, the catalysts were dried in a rotary vacuum evaporator at 100 °C for 45 min and were not calcined.

The nominal loading ($MoO_3/(MoO_3+MgO)$) corresponded to the amount of $(NH_4)_6Mo_7O_{24}$ used and the actual loading was determined by AAS (for particles 0.16–0.32 mm) or by electron microprobe analysis (for extrudates).

The series of MoO_3/MgO catalysts with nominal loadings of 3, 7, 11, 15, 19, and 23 wt.% was prepared by impregnation of 0.16–0.32 mm MgO particles at room temperature. About 15 ml of methanol per 1 g of support was used. The impregnation time was 14 days with occasional gentle stirring. The closed impregnation flasks were not gas tight and were open during the stirring. The evolving NH_3 diffused freely into the surrounding atmosphere.

Extrudates of MgO were impregnated with nominal loadings of either 15 or 30% MoO_3, temperatures of either 25 or 65 °C and impregnation times of 2–480 h; for the combinations of these variables used see Results and discussion. About 3–5 g of the MgO extrudates were used for each preparation. The amount of methanol was 15 and 6 ml per 1 g of MgO for impregnation temperatures of 25 and 65 °C, respectively. The impregnation at room temperature was performed in Erlenmeyer flasks with occasional stirring (every 20 and 40 min in the impregnation time intervals of 0–2 and 2–7 h, respectively, and 3–5 times per day in the impregnation time interval from 7 h until the end of impregnation). The impregnation at 65 °C was performed in boiling methanol under a reflux condenser. From time to time (each 10–15 min up to an impregnation time of 2 h and each 30–60 min thereafter) a gentle stream of air was introduced into the slurry *via* the condenser by a Teflon tube in order to remove the accumulated NH_3 *via* the condenser.

The nominal loading of the catalyst prepared by impregnation of MgO powder in the kneaded paste was 15% MoO_3. The MgO support (40 g, particles 0.16–0.32 mm) was ground in an electric motor driven agate mortar for 10 min. $(NH_4)_6Mo_7O_{24}$ was added and after grinding for 5 min methanol was added in such an amount (about 80 ml) that a thick paste was formed. This was ground (kneaded) for another 15 min then transferred into a round bottomed flask. The surface of the paste was covered by methanol (5 ml) and the flask was heated without mixing at about 60 °C under a reflux condenser for 6 h. After standing overnight at room temperature it was dried in a rotary vacuum evaporator for 2 h. The resulting mass was crushed and sieved to the particle size fraction of 0.16–0.32 mm. The actual loading was equal to the nominal loading because there was no separation of support and the remainder of the impregnation slurry.

Reference MoO_3/Al_2O_3 catalyst

Industrial application of the BASF M8-30 catalyst is the hydrorefining of crude benzene by the BASF-Scholven process. It contained 15% MoO_3 and its surface area (after outgassing at 350 °C) was 240 $m^2\ g^{-1}$.

Surface area

Surface area measurement by adsorption of nitrogen using the dynamic flow method[15] was always performed immediately after the last preparation step (calcination of MgO or drying of MoO_3/MgO), either without any *in-situ* pretreatment ($SA_{F,25}$) or after *in-situ* recalcination for 40 min at 350 °C in a flow of air ($SA_{F,350}$). Selected samples were measured by the conventional static method using a Micromeritics ASAP 2010 instrument after *in-situ* outgassing at 350 °C under vacuum ($SA_{S,350}$).

Electron microprobe analysis

Distribution profiles of Mo in extrudates were obtained using a JEOL JXA electron microscope equipped with the ED analyser EDAX PV 9400. The extrudate was fitted into a hole in a metallic disc and its profile was scraped to the level of the disc using a razor blade, with removal of the dust formed by a water jet pump. Each point in the graphs shown below represents the average loading of a 200 × 200 μm square with the centre of the square at the distance from the extrudate centre plotted on the *x*-axis.

Hydrodesulfurization activity

HDS activity was tested using benzothiophene, BT, reaction in a flow reactor at a pressure of 1.6 MPa and temperatures of 300, 330 and 360 °C. The details of the experimental procedure have been presented elsewhere.[11] The catalysts were not calcined and were presulfided *in-situ* (1 h at 400 °C in a flow of H_2S/H_2 (1/10)). It was checked that calcination (350 °C, 1.5 h) and longer presulfidation (4 h at 400 °C) has no effect on the activity as compared with the non-calcined catalysts sulfided for 1 h at 400 °C. The reaction products were dihydrobenzothiophene, DHBT, and ethylbenzene, EB. The overall conversion of BT at fixed space–time was used as an activity index in the previous paper.[11] However, the kinetic measurements in the present work were more detailed and it was possible to evaluate rate constants. The dependence of the reaction mixture composition (molar fractions of BT, DHBT and EB) on space–time was measured over the whole range of BT conversion (0–100%) for the reference MoO_3/Al_2O_3 catalyst and selected MoO_3/MgO samples. The curves were well fitted by the scheme of four pseudo first-order rate equations (BT to DHBT, DHBT to BT, BT to EB and DHBT to EB). However, none of the corresponding four rate constants is a proper index of activity and it is not possible to combine them into a single activity parameter. However, it was found that the disappearance of BT can be described by a first order equation in good approximation and the corresponding rate constant k_{BT} was used for activity evaluation. Ranking of catalysts according to BT disappearance was the same as that according to EB formation because the selectivity to DHBT formation was very similar for all catalysts (including the reference catalyst): experimental points for all catalysts plotted,using the coordinates of conversion of BT to DHBT *versus* overall conversion of BT to DHBT and EB formed within experimental error one smooth curve.

Results and discussion

Surface area

Surface areas of various batches of supports and catalysts obtained by the flow method are summarised in Table 1. The important proof of the MgO texture stability during impregnation was that the values of $SA_{F,25}$ of the catalysts were similar to the values of $SA_{F,350}$ of the support. Some variation in the surface areas of various batches of extrudates and of various catalysts is explained by the known extreme sensitivity of the measurement of surface areas of MgO based samples to

Table 1 Surface areas of supports and catalysts

Sample	Surface area/m^2 g^{-1} $SA_{F,25}$	$SA_{F,350}$
Particles 0.16–0.32 mm		
MgO	190	210
MoO_3/MgO	170–190	200–220
Extrudates 2.6 mm		
MgO	220–240	230–270
MoO_3/MgO	210–240	230–270
Kneaded paste		
MgO	205	215
MoO_3/MgO	195	215

storage and manipulation conditions.[13,16–19] The conclusions of the present work are not influenced by this variation. For a more detailed discussion of the peculiarities of surface area measurement of MgO based materials see ref. 11.

The results of static measurements ($SA_{S,350}$) of supports and selected catalysts were in good agreement with data from the flow method and they also showed that the typical volume of mesopores (radius smaller than 35 nm) was about 0.6 cm^3 g^{-1} and the volume of micropores (radius smaller than 1 nm) determined by the *t*-plot method was not very important (0.01–0.02 cm^3 g^{-1}).

Impregnation at room temperature

Impregnation at room temperature would be more convenient than the impregnation in boiling methanol described in the previous paper.[11] The impregnation time at the boiling point of methanol was determined by titration of evolved NH_3 and it was several hours (5 h for 0.16–0.32 mm particles and loading of about 10–15% MoO_3). It was found in the present work that the time needed at room temperature was several days, depending on the support particle size and the loading. The difference between the impregnation rates at 25 and 65 °C is well illustrated by Fig. 1 concerning the impregnation of extrudates. For instance, with a nominal loading of 15% MoO_3, the actual loading at the second point from the extrudate geometrical surface and after an impregnation time of 6 h was about 1 and 16% at 25 and 65 °C, respectively.

It is concluded that impregnation at room temperature is feasible. However, it appeared that the catalytic activity of samples prepared at 25 °C was lower than that of the catalysts impregnated at 65 °C (see below).

Impregnation of extrudates

In the previous work only the 0.16–0.32 mm MgO particles were impregnated. It was found in the present work that slurry impregnation may also be applied to extrudates. For instance, extrudates with an approximately homogeneous nominal loading of 15% were prepared by impregnation at room temperature for 240 h (the curve "15% MoO_3, 25 °C, 240 h" in Fig. 1) and extrudates with an approximately homogeneous loading of about 27% were obtained by impregnation at 65 °C for 20 h (see the curve "30% MoO_3, 65 °C, 20 h" in Fig. 1).

It is concluded that slurry impregnation of extrudates is easily achieved. Moreover, it is seen in Fig. 1 that various profiles of the MoO_3 concentration across the extrudates can be obtained and this might be interesting for some applications of the MoO_3/MgO catalysts.

Impregnation in a kneaded paste

Impregnation in a kneaded paste was tested because it would be the most convenient version of slurry impregnation. Impregnation should be fast because small particles of MgO and $(NH_4)_6Mo_7O_{24}$ are in close contact. The paste can be extruded and no waste solids or liquids are produced.

However, it was found that the HDS activity was somewhat lower than the activity of samples prepared by impregnation of 0.16–0.32 mm particles in boiling methanol (see below).

Rate determining step of slurry impregnation

Slurry impregnation is the process composed of the consecutive steps of dissolution of $(NH_4)_6Mo_7O_{24}$, diffusion of the

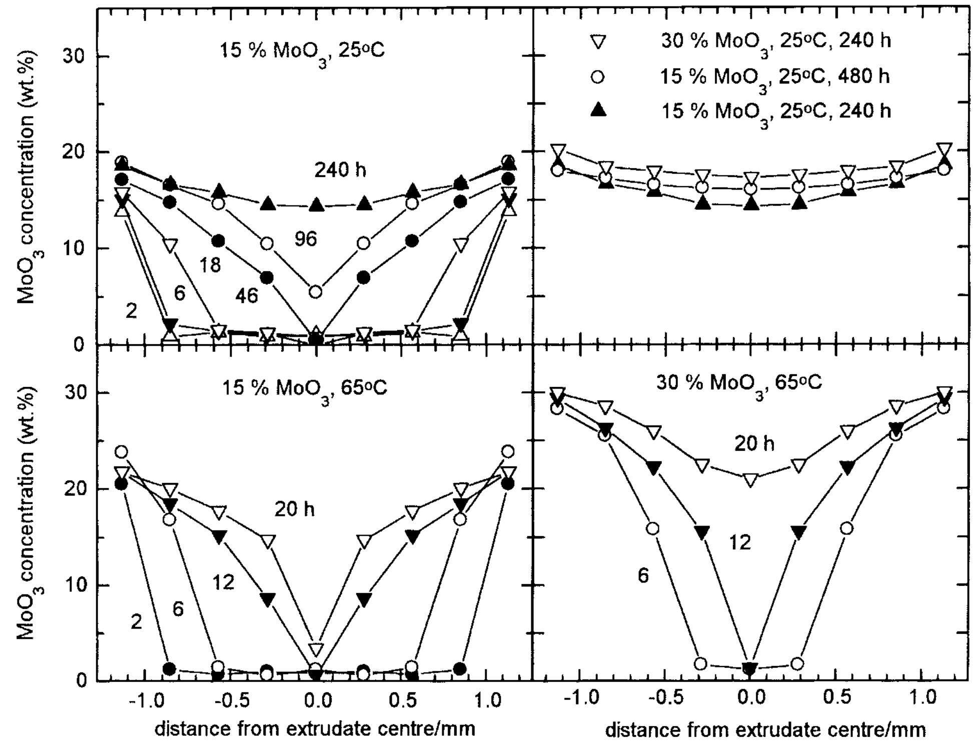

Fig. 1 Profiles of MoO_3 concentration in MgO extrudates impregnated in the $(NH_4)_6Mo_7O_{24}$/methanol slurry at various nominal loadings, impregnation temperatures and impregnation times.

dissolved Mo species to the surface in pores of MgO and the reaction of these species with the MgO surface.

The important point is that with the basic MgO support, NH_3 is evolved already under mild impregnation temperatures of 25–65 °C. In the impregnation of the conventional support Al_2O_3 by a solution of $(NH_4)_6Mo_7O_{24}$, NH_3 is retained in the catalyst even during drying at about 160 °C and it is only removed during calcination at 350–450 °C.

It was found in the previous work[11] that the evolution of NH_3 during impregnation in boiling alcohol (methanol or ethanol) followed an approximately first order rate equation. This kinetics does not allow one to discriminate which of the above consecutive steps is rate determining. However, the kinetics of Mo penetration into MgO extrudates was followed in the present work and the results allow us to make conclusions in this respect. The dependence of the distribution of Mo in the extrudates on the impregnation time was followed by two methods: electron microprobe analysis and visual inspection of fracture of sulfided extrudates.

The data obtained by electron microprobe analysis are shown in Fig. 1. It was observed at both 25 and 65 °C that a relatively sharp Mo concentration wave gradually moved to the extrudate centre as the impregnation time increased.

The colour of fracture of the presulfided extrudates (5% H_2S/H_2 at 400 °C) was inspected using an optical microscope. The loading of Mo can not be evaluated quantitatively in this way. However, qualitatively the results were in full agreement with the electron microprobe analysis. The dark colour of MoS_2/MgO was observed in the whole profile of the homogeneously impregnated extrudates (for instance the curves "30% MoO_3, 25 °C, 240 h" and "30% MoO_3, 65 °C, 20 h" in Fig. 1). A clean white central circle of nonimpregnated MgO and the dark ring of MoS_2/MgO around it were observed for the incompletely impregnated extrudates (for instance the curves "15% MoO_3, 65 °C, 20 h" and "15% MoO_3, 25 °C, 6 h" in Fig. 1). The proportion of the dimensions of the white circle and dark ring corresponded to the profiles in Fig. 1 determined by electron microprobe analysis.

The above results indicate that either dissolution of $(NH_4)_6Mo_7O_{24}$ or transport of dissolved species to the MgO pores was the rate determining step of the impregnation. The surface reaction of dissolved $(NH_4)_6Mo_7O_{24}$ with MgO is clearly not only thermodynamically favoured but also fast. If the surface reaction were the rate determining step, the loading of Mo would be always about the same across the extrudate and it would gradually increase from zero to a saturation value during impregnation (the profiles at various impregnation times would be approximately lines parallel to the x-axis).

Maximum MoO_3 loading achievable by slurry impregnation, and the concept of monolayer

Molybdena supported over various supports such as Al_2O_3, TiO_2, ZrO_2 and MgO belongs to the class of "monolayer type catalysts".[10,20–22] In an idealised model situation, the support surface is gradually covered by a unimolecular layer of molybdena species as the molybdena loading is increased. At the "filled monolayer loading", the support surface is completely covered by a monolayer of molybdena and three dimensional (bulk) molybdenum compounds are as yet absent at the surface. Further increase of the loading leads to the formation of three dimensional molybdenum compounds.

An important parameter frequently studied in the field of monolayer catalysts is the area per Mo atom at filled monolayer, AMAFM, measured in $nm^2\ atom^{-1}$. The methods of AMAFM determination can be divided into three groups.[22] According to the concept of "theoretical geometry monolayer", AMAFM was calculated from the density of MoO_3 or the effective ionic radii in MoO_6 octahedra. According to the concept of "saturated adsorption monolayer", AMAFM was evaluated from saturated adsorption of molybdena species in the gas or liquid phase. According to the concept of "uppermost dispersion capacity monolayer" the filled monolayer loading was determined from the dependence of various properties of Mo/support samples on the Mo loading. The values reported in the literature for alumina supported catalysts using the above three concepts are summarised in Table 2.

No previous data on AMAFM for MgO supported Mo catalysts are available in the literature. A value of 0.20–0.22 $nm^2\ atom^{-1}$ was found experimentally by combination of LRS and XPS over $MgAl_2O_4$ support.[23]

The system MoO_3/MgO seems to differ from other systems such as MoO_3/Al_2O_3, MoO_3/ZrO_2 and MoO_3/TiO_2 by virtue of the relatively strong tendency of Mo ions to diffuse into subsurface layers of MgO during calcination.[9]

Maximum MoO_3 loading. The present new slurry impregnation is a special case of "equilibrium adsorption impregnation" methods[24] for the preparation of supported molybdenum catalysts. The common feature of these methods is that the deposited amount is limited by the sorption capacity of the support for the deposited species under the given conditions. In the present case the suspended $(NH_4)_6Mo_7O_{24}$ dissolves and reacts with the MgO surface until the saturation of the surface.

In the previous paper,[11] only catalysts with a nominal loading of 13% MoO_3 were prepared. In the present work, the saturated deposited amount of MoO_3 was studied using impregnation of extrudates and the results are shown in Fig. 1.

The movement of the Mo concentration wave into extrudates seen in Fig. 1 is analogous to the movement of the concentration wave through the column in frontal chromatography. After a certain time the Mo concentration in the layers near the extrudate surface is not changed with time. These surface layers are saturated (under given conditions) and the dissolved $(NH_4)_6Mo_7O_{24}$ diffuses through them into layers closer to the extrudate centre. The measurement shown in Fig. 1 is a very objective way of determining the saturated loading.

It is seen in Fig. 1 that the saturated loading at 25 °C was about 18–20% MoO_3 (the curves "15% MoO_3, 25 °C, 240 h", "15% MoO_3, 25 °C, 480 h" and "30% MoO_3, 25 °C, 240 h"). Using the mean value of $SA_{F,350}$ of 250 $m^2\ g^{-1}$ for the extrudates, saturated loadings of 18 and 20% MoO_3 correspond to AMAFM values of 0.28 and 0.24 $nm^2\ atom^{-1}$, respectively. These values fall well into the range of AMAFM values of 0.15–0.39 $nm^2\ atom^{-1}$ reported in the literature for alumina supported catalysts (see Table 2). They also correspond well to the value of 0.24 $nm^2\ atom^{-1}$ found in our work[22] concerning the preparation of MoO_3/Al_2O_3 catalysts by the adsorption of molybdic acid. It is concluded that at 25 °C the reaction between $(NH_4)_6Mo_7O_{24}$ and MgO is limited to the surface of pores and a monolayer of molybdena species of similar density as in Al_2O_3 supported catalysts is formed. It seems that the penetration of molybdena into subsurface layers of MgO pores (resulting in the formation of bulk $MgMoO_4$) does not occur at 25 °C.

However, it is seen in Fig. 1 that the saturated deposited amount at 65 °C is considerably higher than at 25 °C. A

Table 2 Area per Mo atom at filled monolayer, AMAFM, reported for MoO_3/Al_2O_3 catalysts by various authors[a]

Concept of filled monolayer evaluation	AMAFM/$nm^2\ atom^{-1}$
Theoretical geometry[b]	0.15–0.21
Saturated adsorption	0.17–0.24
Uppermost dispersion capacity	0.19–0.39

[a]For a summary of more details and references see ref. 22. [b]The values are independent of support by definition.

homogeneous distribution was not achieved with a nominal loading of 15% MoO_3 because of the limited availability of Mo. All suspended $(NH_4)_6Mo_7O_{24}$ was consumed but the Mo concentration in the extrudates centre was only about 3%. Molybdenum species were retained in the outer layers of the extrudates where the actual loading was higher than the nominal loading (curve "15% MoO_3, 65 °C, 20 h" in Fig. 1).

Increasing the nominal loading to 30% MoO_3 at 65 °C resulted in a considerable increase of the saturated loading to about 27–30% MoO_3 (the curve "30% MoO_3, 65 °C, 20 h" in Fig. 1). Using the mean value of $SA_{F,350}$ of 250 m^2 g^{-1} for extrudates, the saturated loadings of 27 and 30% MoO_3 correspond to AMAFM values of 0.16 and 0.13 nm^2 $atom^{-1}$, respectively. These values are already rather outside the range of AMAFM values of 0.17–0.39 nm^2 $atom^{-1}$ found experimentally for Al_2O_3 supported catalysts (see Table 2). It might be concluded that the observed loading of 27–30% MoO_3 is not compatible with the concept of monolayer and that subsurface layers of MgO take part in the reaction at 65 °C. This seems to be a new interesting observation. It is true that the tendency of Mo ions to diffusion into the bulk of MgO[9] or to "incorporation into the MgO matrix"[4,10] was reported in the literature, but this concerned calcined catalysts. However, the catalysts studied in Fig. 1 were measured in dried non-calcined form.

Test of monolayer formation by activity measurement. According to the concept of monolayer formation, the dispersion of molybdena is constant and the catalytic activity per gram of catalyst increases linearly with loading in the range from zero to filled monolayer loading. For instance, we have observed such behaviour for HDS over MoO_3/Al_2O_3 catalysts prepared by slurry impregnation with molybdic acid.[22] At loadings above filled monolayer loading (not achievable by equilibrium adsorption impregnation methods) the dispersion of molybdena decreases and the curve activiry *versus* loading deviates from linearity (activity per gram of catalyst increases less steeply or even decreases).

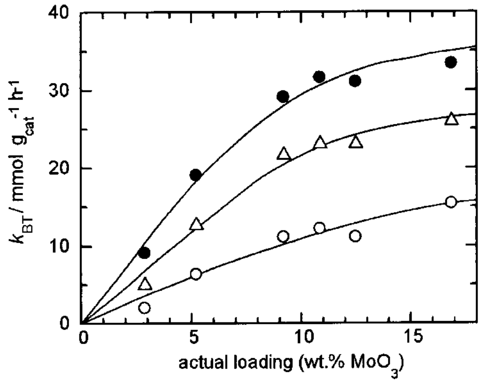

Fig. 2 Dependence of hydrodesulfurization activity on actual loading for the MoO_3/MgO catalysts prepared by the slurry impregnation of 0.16–0.32 mm MgO particles at room temperature; open circles 300 °C, triangles 330 °C, closed circles 360 °C.

The dependence of the HDS activity on the loading was measured using the series of MoO_3/MgO catalysts prepared by impregnation of 0.16–0.32 mm particles at 25 °C and the results are shown in Fig. 2. The saturated adsorption loading observed in that series was about 17% MoO_3 (for the catalyst with a nominal loading of 23% MoO_3) and this agrees reasonably well with the saturated adsorption loading of 18–20% MoO_3 determined in the impregnation of extrudates at 25 °C. However, the activity curves in Fig. 2 tend to deviate from linearity already in the range of loading of 10–15% MoO_3.

It is speculated that this discrepancy is caused by the increased temperature during sulfidation. It is assumed that all Mo is located at the surface after drying of the catalysts prepared at room temperature. However, part of the Mo diffuses into the bulk of MgO during sulfidation at 400 °C and this decreases the effective surface loading as compared with the overall actual loading plotted in Fig. 2. The tendency of Mo to diffuse into the bulk of MgO increases with its surface concentration and that is the reason for the deviation of the curve activity *versus* loading from linearity.

HDS activity

The HDS activity is summarised in Table 3 (as for extrudates, only saturated catalysts were measured). The compared catalysts differed somewhat in surface area and in loading. However, it is seen that, irrespective of these factors, the catalyst prepared from 0.16–0.32 mm particles at 65 °C exhibited the highest activity. A detailed explanation of this point is not available at present. However, it seems that the important point might be that the efficiency of evolved NH_3 removal during preparation of this sample was much higher than for other catalysts. In conventional aqueous impregnation the local pH near the surface is an important factor influencing the structure of the deposited molybdena species and lowering the pH promotes the adsorption of molybdate anions (see for instance refs. 10, 24–26). However, further work is required to clarify the role of ammonia in the present non-aqueous slurry impregnation.

Conclusions

The reaction between MgO and $(NH_4)_6Mo_7O_{24}$/methanol slurry was used for the deposition of molybdena over high surface area MgO without deterioration of texture of this water sensitive support. Various forms of MgO from powder to extrudates were impregnated at mild temperatures of 25–65 °C. Impregnation times were 5–240 h depending on the loading, support particle size and temperature. The saturated loading achievable at 25 °C corresponded to filled monolayer formation of similar density as observed in the literature for alumina support. However, the high saturated loading obtained at 65 °C suggested that subsurface layers of MgO participate in the impregnation reaction at this temperature. Relatively easy diffusion of Mo ions into subsurface layers of

Table 3 Activity of MoO_3/MgO catalysts in HDS of benzothiophene at 330 °C

	Loading/wt.% MoO_3		k_{BT}/mmol h^{-1} g^{-1}	
Sample	Nominal	Actual	per g of catalyst	per g of MoO_3
Particles, 25 °C	23	17	26	153
Particles, 65 °C [a]	13	11	44	398
Extrudates, 25 °C	15	15	21	135
Extrudates, 65 °C [b]	30	27	30	111
Kneaded paste, 65 °C	15	15	30	199
Reference MoO_3/Al_2O_3	—	15	38	256

[a]Prepared in a previous paper.[22] [b]Mean value, see Fig. 1.

MgO was also indicated by the non-linear dependence of HDS activity *versus* loading. The shapes of Mo concentration profiles across extrudates at various impregnation times proved that dissolution of $(NH_4)_6Mo_7O_{24}$ or its diffusion, and not its surface reaction, was the rate determining step of the slurry impregnation. The hydrodesulfurization activity of the best MoO_3/MgO sample was similar to the activity of the conventional industrial MoO_3/Al_2O_3 catalyst. The effective removal (by flow of air) of the NH_3 evolved during impregnation seems to be important for high hydrodesulfurization activity.

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