High surface area MoO_3/MgO: preparation by the new slurry impregnation method and activity in sulphided state in hydrodesulphurization of benzothiophene

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High surface area MoO_3/MgO was prepared by the reaction of MgO (250–300 $m^2\,g^{-1}$) with a slurry of ammonium heptamolybdate in methanol or anhydrous ethanol at the alcohol boiling point. The low solubility of ammonium heptamolybdate was sufficient for its gradual transport to the support surface: molybdena species were deposited and ammonia was evolved. Catalytic activities in the hydrodesulphurization of benzothiophene of the MoO_3/MgO samples were comparable to the activity of the reference commercial MoO_3/Al_2O_3 catalyst.

Keywords: MoO_3/MgO catalyst, hydrodesulphurization, slurry impregnation, benzothiophene

1. Introduction

Supported MoO_3 is a catalyst or catalyst precursor in a number of reactions. The type of the support is an important variable influencing its catalytic properties. The systems of MoO_3 supported over Al_2O_3, SiO_2, TiO_2, ZrO_2, active carbon, and MgO were intensively investigated in literature.

Molybdena supported over MgO was evaluated in the anaerobic oxidation of butane to butadiene [1], oxidative dehydrogenation of ethylbenzene to styrene [2], oxidative dehydrogenation of butane to butadiene [3,4], oxidative dehydrogenation of propane to propene [5–7], and after presulphidation in hydrodesulphurization (HDS) [8,9]. A number of papers analysed the structure of this catalyst by various physico-chemical methods without testing its catalytic properties [10–14].

The present work deals with the MoO_3/MgO system in connection with HDS over Mo, Co–Mo, and Ni–Mo sulphide catalysts. Alumina is the conventional support used in industrial HDS in the production of liquid fuels and in petrochemistry. However, the catalysts supported over SiO_2, TiO_2, ZrO_2, zeolites, and active carbon were studied with the aim of better understanding the role of the support in HDS catalysis and developing better industrial catalysts (for review see [15,16]).

Molybdenum-based sulphide catalysts supported over MgO have not been studied often, probably mainly because the reported HDS activity was low. The activity of the Mo/MgO catalyst was about 26 and 47% of the activity of the corresponding Mo/Al_2O_3 sample in the HDS of benzothiophene [8] and thiophene [9], respectively. However, further research seems to be interesting for three reasons: (i) Other supports of sulphide catalysts studied in literature were mostly acidic, amphoteric, or neutral. Experience with basic MgO may contribute to the theory of support effects in hydrotreating catalysis. (ii) The interaction of acidic MoO_3 with basic MgO would lead to the formation of a strongly bound monolayer of molybdenum oxidic species and this may be favourable for the formation of highly dispersed sulphide species after sulphidation. (iii) Coking of the surface inhibits the activity of alumina-supported catalysts. Acidity of the support promotes coking and it is expected that coking will be slow over MgO-supported catalysts.

The low activity of magnesia-supported sulphide catalysts reported in literature seems to be the result of improper catalyst preparation [17]. The application of the conventional impregnation with an aqueous solution of ammonium heptamolybdate (AHM) commonly used for alumina supports is not suitable for magnesia. The texture of high surface area MgO is deteriorated during aqueous impregnation because it is easily transformed to low surface area $Mg(OH)_2$. It was found that this complication could be eliminated by non-aqueous impregnation [17]. In the preparation of a Ni–Mo/MgO sulphide catalyst, molybdenum and nickel were deposited from the solutions of AHM and nickel nitrate in dimethylsulfoxide and methanol, respectively. The activity of the resulting catalyst in HDS of thiophene [17] and benzothiophene [18] was comparable to the activity of a commercial Ni–Mo–P/Al_2O_3 (Shell 324) catalyst.

However, the use of dimethylsulfoxide as a solvent for AHM is inconvenient for its high boiling point (189 °C). The purpose of the present work is to show that molybdena can be deposited using the slurry (not solution) of AHM

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in methanol or ethanol. The activity of MoO_3/MgO catalysts prepared by the present new method was tested in the HDS of benzothiophene. The reference catalyst was a commercial MoO_3/Al_2O_3 sample.

2. Experimental

High surface area MgO was prepared from low surface area commercial MgO (Labora, Czech Republic, grade "light") by the hydration–dehydration treatment (e.g., [19]). The slurry of MgO (280 g) in water (2500 ml) was heated at 80 °C for 2.5 h. It was filtered and dried at room temperature until constant weight. Drying at room temperature leads to a harder solid than drying at increased temperature. It was crushed to particle size of about 5 mm and calcined in a tubular reactor in a stream of air with temperature program: 95 °C/h from room temperature to 400 °C, 1 h at 400 °C. It was crushed to 0.16–0.32 mm particle size fraction. It was calcined once more immediately before the catalyst preparation: 10 min from room temperature to 390 °C, 70 min at 390 °C.

The reaction between the slurry of AHM in alcohol and MgO was performed in a two-neck pear-shaped flask equipped with a condenser and a narrow tube (i.d. 2 mm) with the nozzle near the bottom of the flask. The outlet of the condenser was connected to two gas-washing bottles in series containing diluted sulphuric acid and with a water jet pump. The nominal loading was 12.7 wt% MoO_3 per gram of dried (2 h at 350 °C) catalyst. The support (3 g), ammonium heptamolybdate (Lachema, content of MoO_3 67%, 0.651 g, finely ground in an agate mortar) and methanol or anhydrous ethanol (40 ml) were placed into the flask and it was heated at boiling point of the alcohol. The gentle stream of air was sucked through the apparatus in order to mix the slurry and to transport the evolved ammonia to the washing bottle. In intervals of time of about 30–60 min, the washing bottle was replaced by a fresh one and absorbed ammonia was determined by acido-basic titration.

Several runs of the reaction between AHM and MgO were done to obtain information about the kinetics of the ammonia evolution. The reaction was followed for about 6–7 h in these cases. The conversion of AHM, α, was defined: $\alpha = n_{\mathrm{NH_3}}/n^0_{\mathrm{NH_3}}$, where $n_{\mathrm{NH_3}}$ is the integral (from the beginning of the experiment to the given time) number of moles of NH_3 determined by the titration and $n^0_{\mathrm{NH_3}}$ is the number of moles of NH_3 in AHM used.

Other runs of the reaction between AHM and MgO were performed to prepare the catalyst samples for activity testing. The reaction time was about 4–5 h in these cases. The catalyst was dried in a rotary vacuum evaporator for 1 h at 100 °C and it was not calcined. It was sieved to 0–0.16 and 0.16–0.32 mm particle size fractions. The fraction 0.16–0.32 mm (about 70% of the total weight) contained 8–11% MoO_3 (determined by AAS) and it was used in catalytic experiments. The *in situ* pretreatment before the surface area and catalytic activity measurements is described henceforward.

The water content in the starting methanol and ethanol was determined by Fischer titration and it was 0.13 and 0.30 wt%, respectively. The alcohols after the reaction contained 1.2 wt% of water, because some water was introduced into the system with crystalline AHM and air bubbled through the mixture.

The reference catalyst was the MoO_3/Al_2O_3 catalyst BASF M8-30. Its industrial application is the hydrorefining of crude benzene by the BASF-Scholven process. The content of MoO_3 (measured by AAS) and surface area (after drying at 350 °C) found in the present work were 15% and 240 $m^2\,g^{-1}$, respectively. The catalyst was crushed to 0.16–0.32 mm particles size fraction.

Surface area was measured by the dynamic flow method [20], either without any *in situ* pretreatment or after *in situ* pretreatment in a gentle flow of air for 1 h at 350 °C. The corresponding values of surface area are designed SA(−) and SA(350), respectively.

HDS activity was tested in a fixed-bed tubular reactor (i.d. 2 mm) with the reaction mixture in the gas phase. The feed was a solution of benzothiophene (BT) in decane (D) and the feed rate, F_i, of BT, D, and H_2 was 7.7, 89, and 595 $\mathrm{mmol\,h^{-1}}$, respectively. The total pressure was 1.6 MPa and each catalyst charge W, 0.2 or 0.5 g, was tested consecutively at the reaction temperature 330, 300, and 360 °C. The condenser at the reactor outlet was kept at 0 °C and the liquid reaction mixture was analysed by gas chromatography. The products of the reaction were dihydrobenzothiophene (DHBT) and ethylbenzene (EB), the amount of other carbon containing products was negligible. The results were evaluated in terms of conversions: overall conversion of BT: $x_{\mathrm{BT}} = (n^0_{\mathrm{BT}} - n_{\mathrm{BT}})/n^0_{\mathrm{BT}}$, conversion of BT to DHBT: $x_{\mathrm{DHBT}} = n_{\mathrm{DHBT}}/n^0_{\mathrm{BT}}$, and conversion of BT to EB, $x_{\mathrm{EB}} = n_{\mathrm{EB}}/n^0_{\mathrm{BT}}$, where n^0 and n are initial and final number of moles, respectively. The catalyst was *in situ* presulphided in a flow of H_2S/H_2 $(1:10)$; the temperature was increased linearly in 45 min from room temperature to 400 °C and it was kept at 400 °C for 1 h. Steady state of the outlet composition was achieved in 20 min after the change of reaction conditions (start of the feed or change of temperature) and no catalyst deactivation was observed during the test (duration of the test at each temperature was about 1 h after the steady state was attained). The material balance between BT in the feed and BT, DHBT and EB in the products was better than ±3%. The catalytic activity of the MgO support alone was negligible.

3. Results and discussion

3.1. Chemistry of impregnation

Magnesium oxide differs from other supports such as Al_2O_3, ZrO_2, TiO_2, active carbon or zeolites in chemical and textural instability under conditions of conventional aqueous impregnation. High surface area MgO is transformed to low surface area $Mg(OH)_2$ in aqueous solutions even at room temperature and this process is promoted by the increased temperature of drying. Partial dissolution of MgO is achieved at the natural pH of AHM aqueous solution [11].

High surface area MgO is stable in methanol [17] but the application of this solvent to the preparation of MoO_3/MgO catalysts has not been considered in literature, because the standard impregnation molybdenum salt, AHM, is practically insoluble in it. However, it was observed in the present work that ammonia is evolved from the slurry of MgO and AHM in an alcohol: litmus paper wetted by water becomes blue in the vapour phase above the slurry. This proves that the very low solubility of AHM in methanol is sufficient for the transfer of AHM to the surface and the reaction between dissolved AHM and MgO takes place. The present new method of preparation of high surface area MoO_3/MgO is based on this observation.

The course of the reaction between MgO and AHM in methanol or ethanol is illustrated by the examples in figure 1. The amount of ammonia evolved corresponded within experimental error to the amount of AHM used (final experimental conversion of AHM, α, was close to 100%). It can be concluded that all molybdena species were transported from solid AHM to an adsorbed layer at the MgO surface.

Two extreme kinetic regimes can be assumed: (i) The solution of AHM is saturated and the rate determining step is the reaction of the dissolved AHM with the surface. (ii) The reaction of dissolved AHM with the surface is very fast and the rate determining step is dissolution of solid AHM. The points for the MoO_3–MgO–alcohol mixtures in figure 1 follow approximately first-order kinetics (see figure 1) that can in principle be compatible with each of the above regimes. More detailed kinetic experiments were outside the scope of the present paper. It is also seen in figure 1 that the reaction was faster in methanol than in ethanol, even when the reaction temperature was lower in the former case. This can be explained by assumed better solubility of AHM in methanol than in ethanol. It was also observed that the reaction rate was not increased when powder of MgO (particles smaller than 0.03 mm) was used instead of MgO of particle size 0.16–0.32 mm. This suggests that the rate of ammonia evolution under our conditions was not limited by the diffusion of AHM into MgO particles.

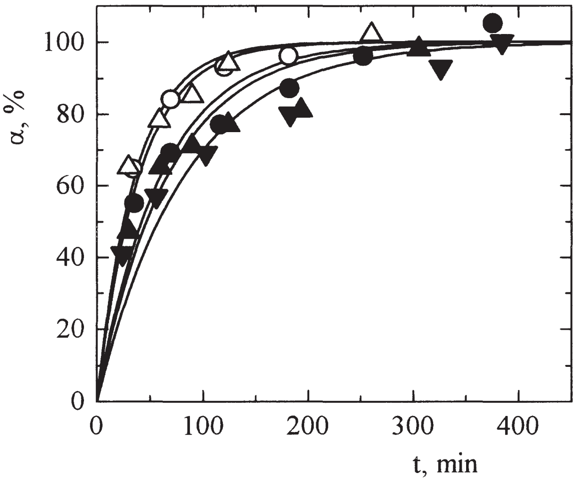

Figure 1. Dependence of the conversion of ammonium heptamolybdate (AHM), α, on the reaction time t, at the temperature of the alcohol boiling point. Open points: slurry AHM–MgO–methanol (2 runs), solid points: slurry AHM–MgO–ethanol (3 runs), curves were obtained by the first-order kinetics.

3.2. Surface area

The pretreatment at increased temperature (in vacuum in the static method or in flow of a gas in the dynamic method) is required before the measurement of surface area of solids by nitrogen adsorption. The surface area, SA, obtained for non-pretreated samples stored in air, SA(−), is lower than the surface area observed for the samples pretreated *in situ* at increased temperature t, SA(t). This is mainly caused by the adsorption or condensation of water in small pores of the sample which blocks the surface for adsorption of nitrogen. For alumina and MoO_3/Al_2O_3 catalysts, for instance, the usual pretreatment temperature is about 250–350 °C and SA(t) is lower than SA(−) by about 20–50%. The cycle of storage on air/*in situ* pretreatment does not change the texture of these materials and the values of SA(−) and SA(t) are not changed by repeating this cycle several times.

However, the texture instability of high surface area MgO caused by its reaction with water complicates the surface area measurement of MgO and MoO_3/MgO samples. Each cycle storage on air/*in situ* pretreatment represents a partial hydration/dehydration cycle (formation of $Mg(OH)_2$/ decomposition of $Mg(OH)_2$) and it may change the area of these materials. Their values of SA(−) and SA(t) are more sensitive to the details of storage and pretreatment than for, for instance, alumina-based materials. This is the reason why the surface area data on MgO-based samples are less reproducible than for less reactive materials.

The surface area of various batches of MgO used in the present work was in the range 250–300 $m^2\,g^{-1}$. The freshly prepared MoO_3/MgO samples (the last operation was drying in a rotary vacuum evaporator) exhibited a surface area SA(−) of about 75–90% of the surface area of the starting support MgO. This proved that the texture of the starting MgO is not deteriorated by the reaction with AHM in the alcohol slurry. Some decrease of surface area mentioned above is explained by adsorption of water (or reaction with water) during the impregnation in the slurry (for the content of water in the impregnation slurry see section 2) and during the manipulation on air before surface area measurement.

The value of SA(−) further slowly decreased during time of storage of the MoO_3/MgO samples in usual laboratory vials which are not completely gas tight. After several weeks, the value of SA(−) of some MoO_3/MgO samples was as low as about 30% of the surface area of the starting MgO. However, the values of SA(350) of freshly prepared or stored MoO_3/MgO samples were in the interval 75–125% of the surface area of the starting MgO.

It is concluded that the texture of the starting high surface area MgO is not deteriorated in the present new method of the deposition of MoO_3 in alcohol slurry.

3.3. Catalytic activity

According to the experience in our laboratory with various alumina- and carbon-supported catalysts, the integral dependencies x_{BT}–W/F_{BT}, x_{DHBT}–W/F_{BT}, and x_{EB}–W/F_{BT} at one initial composition are well described by the consecutive-parallel scheme of four pseudo-first-order reactions (transformation of BT to DHBT is reversible). However, kinetic analysis was not the purpose of the present work. The activity of the MoO_3/MgO catalysts was characterised by the conversions at one or two values of W/F_{BT} at each of the reaction temperatures. This is not enough data for fitting the conversions with the above scheme containing four constants.

However, the data are quite sufficient for the comparison of activity that was the main purpose of the present work. The comparison was made graphically, as presented in figure 2. The full lines (the experimental points are not shown) represent the activity of the reference MoO_3/Al_2O_3 catalyst. The experimental points for the MoO_3/MgO catalysts are compared with these lines (no lines are fitted through these points).

Ten MoO_3/MgO samples were prepared and tested for activity. The content of MoO_3 in the catalyst fraction 0.16–0.32 mm (see section 2) and the catalytic activity were not fully reproducible. The content of MoO_3 was in the range 8–11% MoO_3 and the conversions (x_{BT} or x_{EB}) of MgO-supported samples were in the range of 70–100% of the conversion of the reference alumina-supported catalyst at the given conditions. This limited reproducibility could be connected with mechanical problems during catalyst preparation: the original MgO particles disintegrated partly during the preparation (see section 2). This calls for further experiments to improve this aspect of the preparation.

The data for four typical MoO_3/MgO catalysts are shown in figure 2. It is seen that the activity of the magnesia-supported catalysts is on the same level or somewhat lower than of the reference alumina-supported catalyst. However, the content of MoO_3 in the MgO-supported samples (8–11%) was considerably lower than in the reference catalyst (15%). This high activity of the MoO_3/MgO samples seen in figure 2 is a new result. As mentioned in section 1, previous authors reported that MgO-supported Mo sulphide catalysts are significantly less active than Al_2O_3-supported ones.

Strong chemical interaction is expected between acidic MoO_3 and basic MgO and this may inhibit sulphidation of MoO_3; good sulphidation is known to be favourable for activity in HDS catalysis over Mo-based catalysts [21]. It was checked in the present work that prolongation of the sulphidation time (additional 1 h at 400 °C to the presulphidation procedure described in section 2) has no effect on activity.

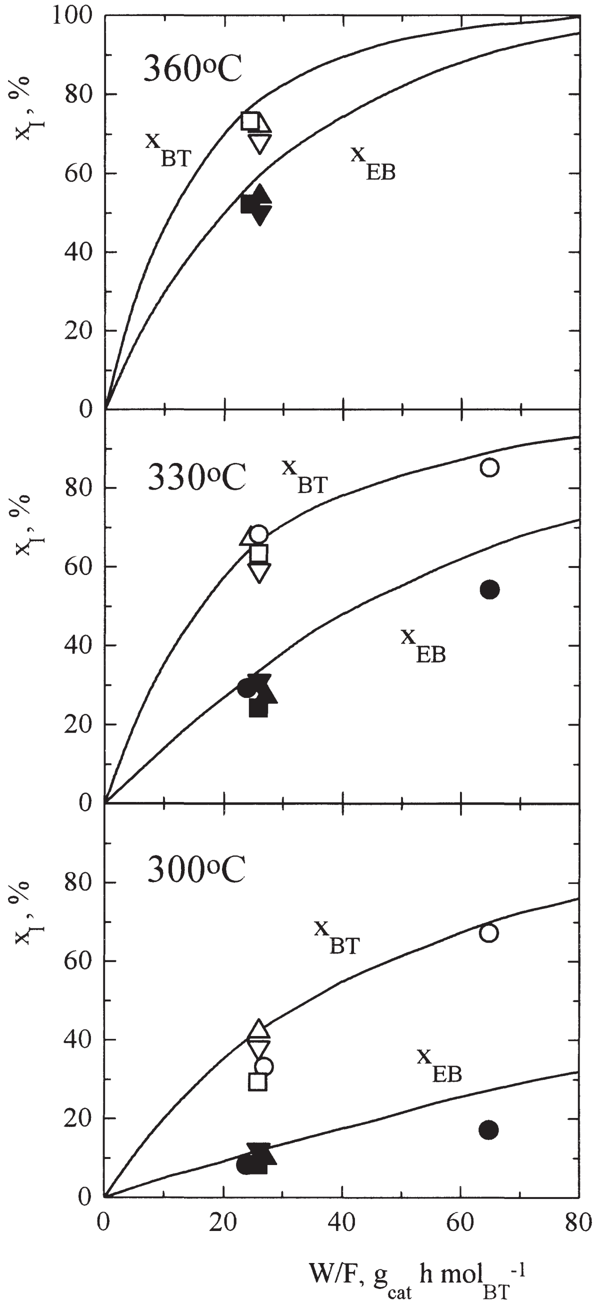

Figure 2. Overall conversion of benzothiophene (BT), x_{BT}, and conversion of BT to ethylbenzene (EB), x_{EB}, versus space time W/F. Lines are for the 15% MoO_3/Al_2O_3 reference catalyst (points are not shown), points are for MoO_3/MgO samples (no lines are drawn). Open points: x_{BT}, solid points: x_{EB}. (△, ▲) 8.5% MoO_3/MgO, methanol; (▽, ▼) 8% MoO_3/MgO, ethanol; (□, ■) 10% MoO_3/MgO, ethanol; and (○, ●) 11% MoO_3/MgO, methanol.

It is believed that the activity of the MoO_3/MgO catalyst prepared by the present method can further be improved by optimisation of MgO texture and MoO_3 loading.

3.4. Selectivity to dihydrobenzothiophene formation

The difference of the curves x_{BT} and x_{EB} in figure 2 corresponds to the formation of intermediate DHBT. It is seen that this difference indicating the selectivity to DHBT for-

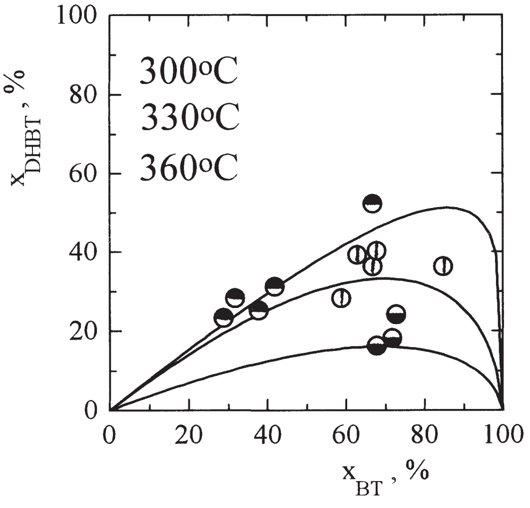

Figure 3. Selectivity to dihydrobenzothiophene (DHBT) in hydrodesulphurization of benzothiophene (BT). Lines are for the MoO_3/Al_2O_3 reference catalyst (points are not shown), points are for the MoO_3/MgO catalysts mentioned in figure 2 (individual catalysts are not distinguished, no lines are drawn). (◓) 300, (⦶) 330, and (◒) 360 °C.

mation decreases with increasing temperature. The selectivity is better evaluated in the x_{DHBT}–x_{BT} plot presented in figure 3. DHBT is formed by hydrogenation and removed by hydrogenolysis of the C–S bond and figure 3 shows that the activation energy of hydrogenation is lower than of hydrogenolysis (selectivity hydrogenation/hydrogenolysis decreases with increasing temperature). This is a general phenomenon in catalysis over sulphides [22,23]. It is concluded from figure 3 that the selectivity hydrogenation/ hydrogenolysis of the Mo/MgO catalysts is about the same or slightly higher than that of the conventional Mo/Al_2O_3 sample.

3.5. Classification of the present preparation method

The present method of preparation of MoO_3/MgO catalysts is a new example of the "slurry impregnation method": a slurry of the impregnation compound is used instead of its solution. The similar principle has previously been used for the preparation of MoO_3/Al_2O_3 [24–26] and MoO_3/C [25,27] catalysts, where a slurry of MoO_3 in water was used instead of a solution of AHM in water.

4. Conclusions

The texture of high surface area MgO support is deteriorated in aqueous impregnation solutions of ammonium heptamolybdate but it is stable in methanol or ethanol. High surface area MoO_3/MgO catalysts were prepared by the reaction between the slurry of ammonium heptamolybdate in these alcohols and MgO. The very low solubility of ammonium heptamolybdate in these alcohols is sufficient for its transport to the surface: molybdena species are deposited and ammonia is evolved. The evolution of ammonia approximately follows first-order kinetics. Catalytic activity in the hydrodesulphurization of benzothiophene of the MoO_3/MgO catalysts prepared by the new method was at the same level as the activity of the conventional MoO_3/Al_2O_3 catalyst and it is believed that it can be further improved. The selectivity to the intermediate dihydrobenzothiophene, indicating the ratio of hydrogenation/C–S bond hydrogenolysis activities, was slightly higher for the MgO-supported catalysts than for the Al_2O_3-supported catalyst.

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