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MoO_3/Al_2O_3 Catalyst: Comparison of Catalysts Prepared by New Slurry Impregnation with Molybdic Acid with Conventional Samples[*]

by A. Spojakina[2], N. Kostova[2], Z. Vít[1] and M. Zdražil[1,]**

[1]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic,*
Rozvojová 135, 165 02 Prague 6-Suchdol, Czech Republic
E-mail: zdrazil@icpf.cas.cz
[2]*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev 11, Sofia, 1113, Bulgaria*

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Alumina-supported molybdena catalysts were prepared by conventional impregnation with $(NH_4)_6Mo_7O_{24}$ (CIM) and by a new slurry impregnation method (SIM). SIM is the reaction of alumina support with the slurry of MoO_3 in water. Two commercial supports were used and the commercial MoO_3/Al_2O_3 catalyst was included for comparison. Maximum amount of MoO_3 deposited by SIM was about 19–20% MoO_3 with the surface area of the support of 260–280 $m^2\ g^{-1}$ and this corresponded to saturation monolayer of similar density as described in literature for CIM catalysts. At the ratios of MoO_3 to Al_2O_3 in the impregnation slurry below saturation monolayer, the pH of the slurry was 3.5–6 (depending on loading) and chemical erosion of alumina was negligible. However, using the large excess of MoO_3 (35% MoO_3), the pH was 2.4–3.4 and chemical erosion of alumina occurred. Silica contained in alumina supports was partly extracted as soluble silicomolybdic anions during SIM. The catalysts were characterized by BET, IR, DRS (UV-vis and NIR), TPR, and catalytic activity in hydrodesulfurization of thiophene. Calcination had no significant effect on the properties of SIM catalysts and this proved that calcination is not needed in that method. All catalysts exhibited features of high monolayer dispersion of molybdena and no significant difference in structure and catalytic properties was observed between SIM and CIM catalysts. This confirmed that SIM is a simple, clean and reliable method of preparation of monolayer type MoO_3/Al_2O_3 catalysts.

Key words: alumina supported molybdenum oxide, molybdenum sulphide catalyst, slurry impregnation, hydrodesulfurization

Molybdena supported on alumina is an important catalyst or catalyst precursor in a number of industrially relevant reactions. The conventional method of its preparation is the impregnation of alumina with a solution of $(NH_4)_6Mo_7O_{24}$ followed by calcination to remove ammonia. However, it was found recently that the introduction of ammonia ions into the system is not necessary. The impregnation can be achieved using a slurry of MoO_3 instead of the solution of $(NH_4)_6Mo_7O_{24}$ and calcination is not needed [1–3].

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[*] Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

[**] Author for correspondence.

The conventional impregnation (CIM) using a solution of $(NH_4)_6Mo_7O_{24}$ can be done either as the "impregnation with excess of solution" or as "incipient wetness impregnation". In both cases, part of $(NH_4)_6Mo_7O_{24}$ is adsorbed during impregnation and part of it is precipitated as bulk particles during drying. The ratio of these two forms depends on the details of the impregnation and influences the dispersion of the molybdena phase after calcination.

Another version of the impregnation using a solution of $(NH_4)_6Mo_7O_{24}$ is the "equilibrium adsorption" or "equilibrium deposition – filtration" method [4]. The impregnation is achieved by adsorption from a relatively large volume of diluted $(NH_4)_6Mo_7O_{24}$ solution and the excess of solution is filtered off before drying; the catalyst can also be washed before drying. The concentration of the $(NH_4)_6Mo_7O_{24}$ solution, remaining in the pores before drying, is low and the precipitation of $(NH_4)_6Mo_7O_{24}$ particles in the pores during drying is minimized.

The new slurry impregnation using MoO_3 (SIM) belongs to the equilibrium adsorption methods. The natural pH of the impregnation slurry of MoO_3 (about 2.8) is below the isoelectric point of alumina support (about 6–8) and this is generally advantageous for adsorption of molybdate ions [5,6]. The precipitation of molybdena during drying is negligible, because the solution in the pores is very diluted (low solubility of MoO_3). As in other equilibrium adsorption methods, the deposited amount of MoO_3 is limited by sorption capacity of the support.

Another method of preparation of MoO_3/Al_2O_3 catalysts is "solid/solid wetting" [7–9]. A fine powder of a MoO_3-Al_2O_3 mixture is heated for several hours at 500–550°C. The important disadvantage of this method is that the support must be in the form of fine powder and that the system has the tendency for the formation of $Al_2(MoO_4)_3$ at the high temperature required. On the other hand, any particle size from fine powder to extrudates or pellets can be impregnated by the SIM and the temperature used is very low.

The previous data on SIM samples, obtained by XRD, XPS and catalytic activity measurements, suggest that this new method is a simple and reliable way to prepare MoO_3/Al_2O_3 catalysts with well-defined, homogeneous and highly dispersed molybdena species [1–3].

The objective of the present work was the detailed comparison of the MoO_3/Al_2O_3 samples prepared by the new SIM method with the CIM laboratory-made and commercial catalysts. Two commercial alumina supports were used. The catalysts were characterized by surface area measurement, IR and UV-vis-NIR DRS spectroscopy, TPR and activity in hydrodesulfurization (HDS) of thiophene. All these techniques have already been extensively applied to conventional MoO_3/Al_2O_3 catalysts and detailed interpretation of the results can be found in previous literature. That is the reason why the discussion of the results in the present work concentrates only on the comparison of the CIM and SIM samples using the results of the above techniques as a "fingerprint" characteristics of the sample.

EXPERIMENTAL

Supports. Properties of the alumina supports used are summarized in Table 1. The extrudates were crushed to the 0.16–0.32 mm particle size fraction and were dried for 2.5 h at 160°C before use.

Common steps in catalysts preparation. The samples prepared by the conventional impregnation method with the $(NH_4)_6Mo_7O_{24}$ solution and the samples prepared by the slurry impregnation method with the MoO_3 slurry are designed by CIM and SIM acronyms, respectively. The temperature of drying in a rotary vacuum evaporator was about 95°C and the pressure was about 4–6 kPa. MoO_3 (Fluka, better than 99.5%) was ground in an electric motor driven agate mortar for 75 min before use. CIM samples and a portion of each SIM sample were calcined in a tubular flow reactor in a stream of air with the temperature program: ramp 10°C min^{-1} to 400°C and dwell at 400°C for 2 h. Before the SIM impregnation, the support was washed and decanted (five times with about 50 ml of water) in order to remove fine particles.

SIM catalysts. The mixture of Al_2O_3 and MoO_3 (amounts are shown in Table 2) in water (60 ml) was heated to about 95°C under reflux condenser for 5 h with occasional shaking. It was left standing at room temperature overnight and heated for another 2 h. After standing 1 h at room temperature, the turbid liquid was separated from the impregnated support by repeated decantation. The catalyst was washed three times with about 25 ml of cold water (5°C) in order to separate any fine particles of the unreacted MoO_3 and eroded support. All these turbid liquids were combined and dried in a rotary vacuum evaporator and the resulting powder was dried in a drying box. Its weight and composition (ICP analysis) were determined. The catalyst was dried in rotary vacuum evaporator until became loose and then it was dried 3 h at 160°C in a dry box. One part of it was calcined at 400°C under the conditions described above. The catalysts were named according to the example: 5SIMAkzo is the catalysts with the nominal loading of 5% MoO_3 ($MoO_3/(MoO_3+Al_2O_3)$) prepared from the Akzo support and dried at 160°C; 5SIMAkzo(calc) catalyst is the 5SIMAkzo sample calcined at 400°C.

The pH of the slurry was measured in about 1–1.5 h intervals during the impregnation. The flask with the slurry was quickly cooled to room temperature with cold water and the measurement took about 5 min.

The time of the SIM impregnation was the same for all catalysts (see above). However, the MoO_3 powder disappeared from the slurry already after about 45–60 and 120–150 min for the samples 5SIM and 15SIM, respectively. A considerable part of MoO_3 still remained unreacted at the end of the impregnation of the 35SIM catalysts (see Results).

With the Akzo support, the liquid in the impregnation slurry was colourless for the 5SIM sample. A transient yellow colour appeared during the first hour of the preparation of the 15SIM catalyst and a permanent yellow colour was observed during the preparation of the 35SIM sample. With the Norton support, the liquid was colourless for the 5SIM and 15SIM catalysts. A yellow colour appeared gradually after two hours of impregnation of the 35SIM sample but this colour was less intensive than for the 35SIMAkzo catalyst.

CIM catalysts. $(NH_4)_6Mo_7O_{24}$ (Fluka, the amount corresponding to the loading 5 or 15%) was dissolved in water (50 ml) at 55°C and alumina (7.5 g) was added. It was left standing for 1 h at room temperature with occasional shaking, dried in rotary vacuum evaporator and calcined as described above.

Reference catalyst. The commercial catalyst Mo/Al_2O_3, BASF M 8-30 was used as the reference point of activity. The catalyst is intended for the refining of crude benzene and its nominal composition is about 15 wt.% MoO_3 according to the catalogue of the producer. The composition found in the present work (AAS) was 14.9 wt.% MoO_3 and the surface area was 210 $m^2\ g^{-1}$.

Catalytic activity. The model reaction was HDS of thiophene (TH) in the gas phase in a fixed bed flow reactor. The test at increased pressure of 1 MPa and the test at atmospheric pressure were performed independently in two different testing units in the co-operating laboratories. The conversion of thiophene was defined as $x(TH) = (n^o(TH) - n(TH))/n^o(TH)$, where n^o and n are the initial and final number of moles, respectively.

In the test at increased pressure, the feed rate of TH, F(TH), and hydrogen, $F(H_2)$, were 0.43 mmol h^{-1} and 1.1 mol h^{-1}, respectively. The catalyst charge, W, was 0.03 g. It was in-situ presulfided by the H_2S/H_2 mixture (1:10) at atmospheric pressure with the temperature program: ramp 6°C min^{-1} to 400°C and dwell 1 h at 400°C. The feed TH/H_2 was introduced at 400°C and 1 MPa. The conversion x(TH) was determined at several temperatures from 400 to 250°C, changing the temperature in steps of 30°C. The conversions were in the range 0.05–0.92, depending on the catalyst and temperature. The test lasted about 9 h and no deactivation of the catalysts was observed: stable conversion was attained after a very short time of about 15 min (needed for stabilization of the reaction conditions).

The test at atmospheric pressure was performed at the reaction temperature of 350°C. The catalyst charge of 0.2 g was heated in a stream of argon for 1.5 h at 350°C, sulfided in a stream of H_2S (in the absence of hydrogen) for 0.5 h at 350°C and flushed with argon for 0.5 h at 350°C. The feed of 6 mol.% of TH in hydrogen was introduced at a rate of 67 mmol h^{-1} and the composition of the reaction products was followed by on-line GC analysis. The conversion stabilized after 2 h and it was monitored for another 2 h on stream. The decrease of the conversion during the first two hours on stream was 10–30 % of the initial activity, depending on loading. No difference between conventional and slurry impregnation samples was observed in this respect (the curves conversion versus time on stream were similar for the corresponding catalysts prepared by the conventional and slurry impregnation method). The conversions x(TH) over various catalysts were in the range of 5–30%.

Catalysts characterization. Surface area was measured by the adsorption of N_2 using the single point flow method [10]. The samples were dried at 350°C for 3 h in stream of air before the measurement.

Temperature programmed reduction (TPR) was performed in a conventional home made apparatus equipped with a TC detector. The quartz reactor was charged with 0.2 g of catalyst and purged with the mixture 5 vol.% of H_2 in Ar (35 ml min^{-1}) for 0.5 h at room temperature. The temperature was increased linearly with 5°C min^{-1} up to 980°C. The water evolved during TPR was removed from the gas stream in a column filled with the molecular sieve Linde 13X and placed upstream of the TC detector. The detector was calibrated by the reduction of CuO samples.

IR spectra were recorded at room temperature on an IFS-25 FTIR spectrometer (Bruker) using KBr pellets (ratio sample/KBr was 1:150). The absorption of the support was compensated by the subtraction of the normalized spectrum of the corresponding amount of the support.

DRS spectra were recorded at room temperature on a Beckman UV 5270 spectrophotometer. Barium sulphate and the alumina support were used for reference in the NIR and UV-vis regions, respectively.

RESULTS AND DISCUSSION

Preparation of catalysts. The area per Mo atom at monolayer coverage of the alumina surface reported by various authors varies in the broad range of approximately 0.15–0.39 nm^2 $atom^{-1}$, depending on the evaluation method [3]. This corresponds to a MoO_3 loading ($MoO_3/(MoO_3+Al_2O_3)$) of 31–15% and 29–14% for the Akzo and Norton alumina, respectively (using surface areas shown in Table 1). So the nominal loadings of 5, 15 and 35 wt.% MoO_3 of the present catalysts were below monolayer, close to monolayer and above monolayer, respectively.

The course of the SIM preparation of the samples 5SIM and 15SIM with the present Akzo and Norton 6175 aluminas (content of SiO_2 see Table 1) confirmed our previous experience with Condea alumina (very low content of SiO_2, 0.02% max.) (ref. [3]) and Norton 6173 alumina (low content of SiO_2, 0.09% max.) (refs [1,2]). The reaction of MoO_3 with the alumina particles was fast at about 95°C and almost quantitative. The mass balance of the impregnation is shown in Table 2. The amount of MoO_3 remaining in the turbid liquid separated from the catalyst after impregnation was negligible, it represented less than 0.4% of the MoO_3 used. The mechanical and chemical erosion of alumina support was also negligible for these samples according to Table 2.

Table 1. Alumina supports used.

Alumina	Surface area, m^2g^{-1}		Content of SiO_2, %		Other impurities (nominal), %
	Nominal	Measured	Nominal	Measured	
Akzo HDS.000.1.5	290	282	0.96	0.36	0.1 Na_2O, 1.3 SO_4
Norton SA 6175	230–290	258	< 0.18	0.09	< 0.02 Na_2O

Table 2. Mass balance during catalyst preparation.

Catalyst	Weight used, g		Solids of separted turbid liquid			
			Weight, g	Composition, %		
	Al_2O_3	MoO_3		MoO_3	Al_2O_3	SiO_2
Support Al_2O_3 Norton						
5SIM	15	0.79	0.02	10	89	1
15SIM	15	2.65	0.06	49	49	2
35SIM	15	8.08	5.24	87	12	1
Support Al_2O_3 Akzo						
5SIM	15	0.79	0.05	13	86	0.4
15SIM	15	2.65	0.18	38	61	0.5
35SIM	15	8.08	5.45	85	14	0.7

However, considerable chemical erosion of the Al_2O_3 support during the SIM preparation of the 35SIM samples was observed. The mass of Al_2O_3 found in the solids of the turbid liquid, separated from the catalyst after impregnation, represented 4.2 and 5.1% of the amount of the support used for the Norton and Akzo samples, respectively (Table 2). This erosion was probably connected with the rather low value of pH developed in the impregnation slurry containing high surplus of MoO_3. It is seen in Table 3 that the pH of the slurry for the 35SIM samples was lower by about one unit than for the corresponding 15SIM samples.

Table 3. The values of pH of the slurries.

Solid in the slurry	pH
MoO_3[a]	2.8
Al_2O_3 Norton[a]	7.3
Al_2O_3 Akzo[a]	6.6
Support Al_2O_3 Norton	
5SIM	5.8–6.1[b]
15SIM	3.5–3.9[b]
35SIM	2.4–2.8[b]
Support Al_2O_3 Akzo	
5SIM	5.5–6.0[b]
15SIM	3.8–4.1[b]
35SIM	3.1–3.4

[a] The ratio solid/water was the same as during catalyst preparation. [b] The order of the values reflects the trend during the time of the SIM impregnation.

The impurities or additives of alumina, such as Na_2O and SiO_2, for instance, might also influence the erosion of the alumina support. The yellow colour of the impregnation liquid observed for some samples in the present work (see

Experimental) can be explained by the formation of well soluble and strongly acidic silicomolybdic acid (or its salts). Its formation by heating the slurry of MoO_3 and SiO_2 is a well-known procedure in preparative inorganic chemistry. The formation of the yellow colour was more intensive for the Akzo alumina that contains more SiO_2 than for the Norton support (see experimental and Table 1).

The dissolution of Al_2O_3 during conventional equilibrium adsorption impregnation with a $(NH_4)_6Mo_7O_{24}$ solution was investigated recently by Carrier *et al.* [11]. It was reported that at a given pH the solubility of Al_2O_3 is strongly promoted by the presence of molybdate anions in the solution. The formation of the mixed $[AlMo_6]$ species resulted in an increase of alumina solubility by several orders of magnitude. This phenomenon might of course occur also in the present SIM method, because this method is related to the conventional equilibrium adsorption method using AHM (see Introduction).

The actual composition of the 5SIM and 15SIM catalysts and CIM catalysts should be the same as their nominal composition, because all amount of the AHM used remained in the CIM catalysts and the mass of the MoO_3 separated after SIM impregnation was negligible (see Table 2). Some samples were analysed by ICP analysis and the nominal and actual contents of MoO_3 were the same within the experimental error of about 10%.

However, the actual composition of the 35SIM samples differed significantly from the nominal composition of 35% MoO_3, because a considerable amount of MoO_3 used was not deposited at saturation equilibrium and was separated from the impregnated support (see Table 2). The actual composition of these samples was calculated from the mass balance in Table 2 and also determined by ICP analysis and similar results were obtained. It was 19 and 19.5 % MoO_3 for the 35SIM Norton and Akzo samples, respectively. The area per Mo atom calculated from these saturated loadings and values of surface area of catalysts given in Table 4 (222 and 287 $m^2\ g^{-1}$, respectively) is 0.28 and 0.35 nm^2 per Mo atom. This is well within the range of values of area per Mo atom at monolayer observed over the conventional alumina supported catalysts by various methods [3].

Table 4. Surface area and relative hydrodesulphurization activity.

Catalyst	Surface area, $m^2 g_{cat}^{-1}$		Activity at 1 MPa[a]		Activity at 0.1 MPa[b]	
	Norton	Akzo	Norton	Akzo	Norton	Akzo
Support Al_2O_3	258	282	–	–	–	–
5CIM(calc)	274	274	0.27	0.42	0.36	–
5SIM	266	285	0.30	0.33	–	–
5SIM(calc)	253	309	0.30	0.43	0.42	0.40
15CIM(calc)	228	240	1.00	1.04	1.00	1.11
15SIM	230	277	1.24	1.36	–	–
15SIM(calc)	229	260	1.00	1.11	1.11	1.11
35SIM	222	287	1.58	1.42	–	–
35SIM(calc)	218	279	1.41	1.42	2.81	1.69

[a] The reference catalyst was the commercial BASF M8-30 sample with BET area of 210 $m^2\ g^{-1}$. [b] The reference catalyst was the 15CIMNorton(calc) sample.

The values of the surface areas of the catalysts are presented in Table 4. They suggest that gradual formation of a monolayer does not change the texture of the supports significantly. No negative effect of the SIM impregnation on the surface area of the supports as compared with CIM impregnation is seen in Table 4.

The data of surface area in Table 4 are normalized to catalyst weight. When normalized to the weight of the support contained in the sample, the values of 266–288 and of 282–350 m^2g^{-1} are obtained for the Norton and Akzo catalysts, respectively. The values for the Norton catalysts are the same as that of the starting support within the experimental error. However, the values for some of the Akzo catalysts are higher than the surface area of the starting support. The 35SIMAkzo and 35SIMAkzo(calc) catalysts exhibited especially high area of 340–350 $m^2g_{sup}^{-1}$ and this might be explained by the formation of some micropores during SIM impregnation (the above mentioned dissolution of alumina might play a role).

Temperature programmed reduction. TPR patterns of the 15SIM and 15CIM samples and of the reference BASF catalyst were measured and selected data are shown in Figure 1 (the data for SIM(calc) catalysts are not shown for simplicity, see below). The reduction of all catalysts proceeded in two temperature regions with maxima near 460 and 870°C. In literature, the low (LT) and high (HT) temperature peaks are usually ascribed to the reduction of the multilayered oligomeric molybdate species and highly dispersed tetrahedrally co-ordinated molybdate groups, respectively [12–14]. No peak or shoulder in the 500–550°C region was observed and this indicates the absence of the bulk MoO_3 and good dispersion of molybdena phase [15,16].

The total amount of moles of hydrogen consumed per Mo atom up to 980°C was in the range of 2.8–3.2 for all 15SIM and 15CIM catalysts prepared in the present work. No significant difference was observed between the SIM and CIM samples with the same support. Taking into account the experimental error (about 7%), it can be concluded that complete reduction of supported MoO_3 to Mo metal was achieved. It is

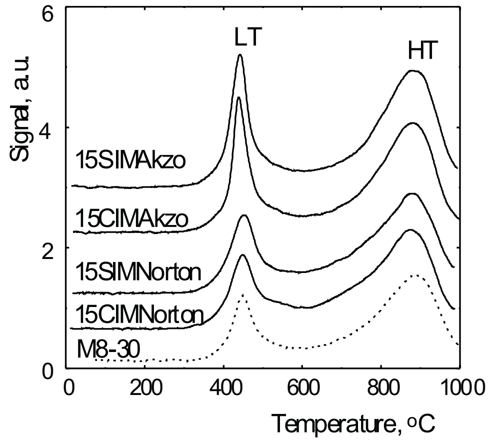

Figure 1. TPR profiles for the MoO_3/Al_2O_3 catalysts.

well known that the degree of reduction of MoO_3/Al_2O_3 catalysts increases with loading and decreases with the temperature of calcination (for instance refs [17,18]). For the above 15SIM and 15CIM samples, the loading was close to monolayer saturation loading and the temperature of calcination (400°C) was relatively low and these are the reasons why high reduction degrees were observed. However, the consumption of hydrogen in TPR of the reference M8-30 BASF catalyst was only 2.3. This suggests a stronger interaction of Mo with the support in the reference catalyst as compared with the catalysts prepared in the present work. The details of the preparation of the reference catalysts are not known, but we assume that it was probably calcined at more severe conditions (longer time, higher temperature) than those used in the present work.

The most important result of TPR experiments was that the reduction patterns (position, height and shape of the LT and HT peaks) of the CIM and SIM samples were practically identical for each alumina support (see Figure 1). This indicates that the simple SIM method using MoO_3 (no ammonia, no calcination) provides the catalysts of the same structure as conventional impregnation with $(NH_4)_6Mo_7O_{24}$.

The catalysts supported over Akzo alumina exhibited a slightly lower position of the LT peak (about 10°C) and a slightly higher ratio of areas of LT/HT peaks (0.47 *versus* 0.40) as compared with the sample supported over the Norton alumina and the commercial sample. This indicates that the amount of polymeric octahedral species is higher in Akzo samples and it might be connected with the higher content of silicomolybdic acid. However, this result was not analysed in detail, because it was not the purpose of the present work to study the effect of detailed alumina support composition on the reducibility of Mo species.

The difference between the TPR spectra of the uncalcined and calcined SIM samples was very small and close to experimental error. However, the tendency was a slight decrease of area of the LH peak (2–5%) and a small increase of the temperature maximum of the HT peak (5–15°C) with calcination. This tendency is consistent with the idea that calcination strengthens the interaction between molybdena species and alumina and makes the reduction little more difficult.

Infrared spectra. The spectra of the catalysts are shown in Figure 2, together with the spectra of model compounds MoO_3 and $(NH_4)_3[Al(OH)_6Mo_6O_{18}]$. The IR spectra of MoO_3/Al_2O_3 catalysts have been measured and discussed in many previous papers of other authors and it was concluded that firstly monomeric and then polymeric molybdenum species are deposited as the Mo loading is increased. The formation of the MoO_3 phase begins when the monolayer coverage is completed [19]. An aluminum heteropolybdate analogue was proved in the polymolybdate phase (ref. [20]) and also in the phase formed by the decomposition of alumina supported phosphomolybdic acid [21]. Recent results also proposed the formation of 6-heteropolymolybdate stabilized by interaction with the alumina support [22].

Characteristic bands of aluminum heteropolymolybdate (450, 660, 900, 955 cm^{-1}, [23]) observed in the spectra in Figure 2 and the comparison of spectra of the catalysts and of the model compound in Figure 2 indicate the formation of heteropolyanion

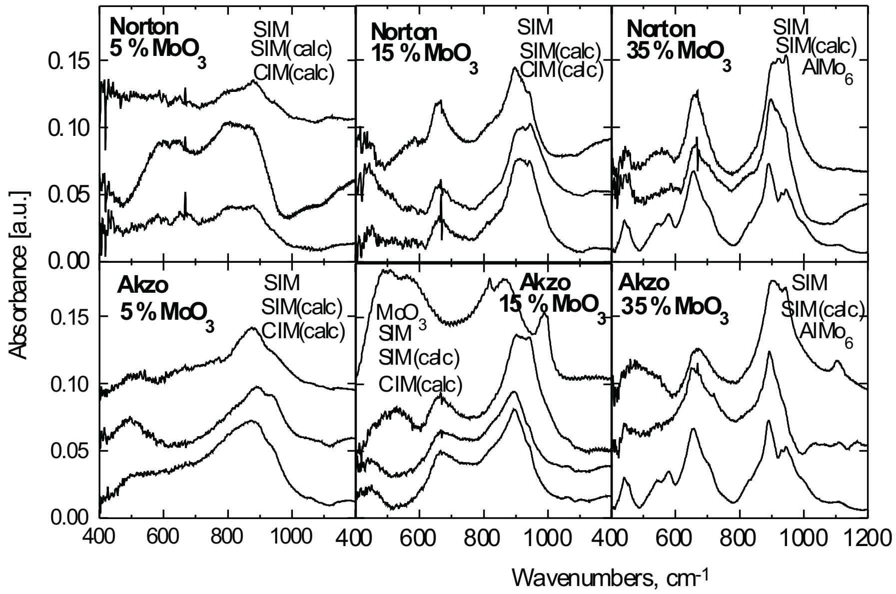

Figure 2. IR spectra for the MoO_3/Al_2O_3 catalysts.

$[AlMo_6O_{24}]^{3-}$ in the catalysts although other Mo species are present (isopolymolybdates, $Al_2(MoO_4)$, MoO_3). The spectra are almost independent of the preparation method. As for the 15 wt.% MoO_3 samples, the spectra of the SIM(calc) and CIM(calc) are practically identical for each support. A certain difference between SIM(cal) and CIM(calc) samples is seen for the 5Akzo catalysts (the peaks at about 500 and 930 cm^{-1} are more intensive for the SIM(calc) than for the CIM(calc) sample), but this difference can be classified as small. The IR spectra thus confirm that the structure of the SIM and CIM catalysts is very similar.

The 15 and 35 wt.% MoO_3 samples supported on the Akzo carrier exhibit weak bands in the region of about 1050–1100 cm^{-1}, which is characteristic for Si–O stretching [24]. Other SiO vibrations in the region below 1000 cm^{-1} are overlapped with the bands of molybdenum species. This region probably also includes the bands of silicomolybdic acid [25]. These spectra features, indicating the presence of Si species, were not observed for the Norton catalysts and this corresponds with the lower content of Si in Norton than in Akzo alumina.

Diffuse reflectance spectra. An intensive absorption in the UV region of about 250–450 nm is observed for all samples. Three phenomena were identified.

(i) No important effect of the type of the preparation procedure on the spectra was observed, the spectra of the corresponding CIM(calc) and SIM(calc) catalysts were essentially identical for each alumina.

(ii) Because there is no distinct maximum in the bands, the comparison of the molybdenum state could be made using the wave length λ_{end} at which the absorption disappears (Table 5). The shift of the absorption end (λ_{end}) to higher wave lengths was interpreted as the result of an increase of octahedral Mo species relatively to tetrahedral ones [26–29]. It is seen in Table 5 for all catalysts that the amount of octahedral species increased with loading. This is in agreement with literature [30].

Table 5. The wave length λ_{end}, [nm], at which the absorption disappears (going from UV to VIS region)[a].

Catalyst	Norton		Akzo	
	Dried	Calcined	Dried	Calcined
5SIM	400	400	400	415
15SIM	420	435	450	470
35SIM	440	460	460	470
5CIM	–	400		415
15CIM	–	440		470

[a] λ_{end} for $(NH_4)_3[Al(OH)_6Mo_6O_{18}]$ is 460 nm.

It is also noted in Table 5 that the value of λ_{end} is systematically higher over Akzo samples than over corresponding Norton catalysts. This indicates that the amount of octahedral species is higher in the Akzo samples and that is probably connected with the higher content of silicomolybdic acid. This conclusion agrees with the TPR results mentioned above.

(iii) It is seen in Table 5 that the λ_{end} is by 10–20 nm lower for the uncalcined than for the calcined SIM catalysts. (The position of the absorption end of the CIM(calc) catalysts was the same as of the corresponding SIM(calc) samples.) It can be concluded in agreement with the literature ([29,31]) that the formation of octahedrally coordinated Mo species increased by calcination.

Catalytic activity. Typical results obtained in the test at increased pressure of 1 MPa are illustrated in Figure 3. The important feature of the data was that no crossing of the curves x(TH) *versus* temperature was observed and activity ranking of catalysts was independent of temperature. It was checked previously that under fixed conditions of the present catalytic test the dependence x(TH) = f [W/F(TH)] follows in

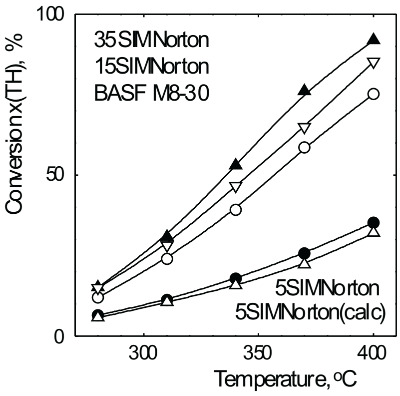

Figure 3. Conversion of thiophene in high pressure test (1 MPa) over sulphided MoO_3/Al_2O_3 catalysts. Order of curves corresponds to order of catalysts names.

the range of x(TH) from 0 to 0.90 a pseudo-first order rate equation with the apparent rate constant k. All catalysts were tested at the same space time W/F(TH) and at several temperatures. Equation (1) can be written for each temperature

$$\ln[1 - x(TH,j)] = [k(j)/k(r)]*\ln[1 - x(TH,r)] \quad (1)$$

where j and r denote the j-th and the reference catalyst, respectively. The commercial catalyst 15% MoO_3 BASF M-8-30 was chosen as the reference catalyst. Straight lines were obtained by plotting the conversions x(TH) at various temperatures according to equation (1). This indicates that the apparent activation energies of the samples tested were the same. The ratios k(j)/k(r) were obtained from the slopes of the lines. They are independent of temperature and characterise the relative activity of the catalysts in the whole range of conversions measured. They are presented in Table 4.

The relative activity in the test at atmospheric pressure was evaluated according to the equation

$$k(j)/k(r) = [\ln(1 - x(TH,j))]/[\ln(1 - x(TH,r))] \quad (2)$$

under assumption of the pseudo first-order kinetics with the rate constant k. The sample 15CIMNorton(calc) was used as the reference catalyst and the values of the relative activity are shown in Table 4.

The catalytic activity data summarized in Table 4 show that the samples prepared by the new SIM procedure posses the same or slightly better activity than the CIM samples prepared by the conventional impregnation with AHM and than the commercial BASF M8-30 catalyst. This is in full agreement with our previous results obtained with another alumina supports and another details of the SIM procedure (preparation at lower temperature of 30–50°C, for instance).

The effect of calcination on the activity of the SIM catalysts has not been systematically investigated previously. The data in Table 4 prove that calcination can be left out in the SIM procedure, because the activity of the uncalcined samples was mostly the same or better than the activity of the calcined catalysts.

CONCLUSIONS

Molybdena was deposited over alumina by simple slurry impregnation method: alumina reacted with the slurry of MoO_3 and calcination was not needed. No significant difference between calcined and non-calcined slurry impregnation catalysts was observed with IR, DRS (UV-vis and NIR), TPR and hydrodesulfurization activity measurements. The slurry impregnation catalysts were compared with the catalysts prepared by conventional impregnation with $(NH_4)_6Mo_7O_{24}$ and no significant difference between the corresponding catalysts was found using the above techniques. With the amount of MoO_3 in the impregnation slurry close to monolayer adsorption capacity of alumina support, the pH of the impregnation slurry was about 3.5–4.1 and chemical erosion of alumina support was not significant. However, a large excess of MoO_3 above monolayer sorption capacity of the support kept the pH of the impregnation slurry at the low level of 2.4–3.4 and considerable chemical erosion of alumina occurred. Silica contained in the alumina carrier was partly extracted into the impregnation slurry by formation of soluble silicomolybdate anions. It is concluded that the reaction between Al_2O_3 and MoO_3 in aqueous slurry is a simple and reliable way to well-defined monolayer MoO_3/Al_2O_3 catalyst.

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