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Reactivity of molybdena with silica and alumina

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Molybdena–alumina and molybdena–silica systems have been prepared by impregnating the support with aqueous solutions of ammonium heptamolybdate (samples I) or by mixing MoO_3 with Al_2O_3 or SiO_2 (samples M), and calcining at 770 K (to decompose the molybdate) and 1100 K (to melt molybdena). In all eight cases the composition corresponds to two monolayers of molybdena. The solids have been characterized by nitrogen adsorption, X-ray diffraction, electronic and infrared spectroscopies, temperature programmed reduction and electron microscopy. Whichever the preparation method, only molybdena is detected on silica, and molybdena and $Al_2(MoO_4)_3$ on alumina. The dispersion of molybdena, however, depends on the preparation method and the nature of the support. Formation of ternary Mo–Al–O compounds is due to support–supported phase interaction, that stabilizes molybdena even upon calcining at 1100 K, while MoO_3 is removed by sublimation from the silica surface, leaving only 6.5% of the original loading. This behaviour can be related to the differences in the acidities of the supports, and then reaction of the more basic alumina with molybdena is easier than reaction with silica, thus accounting for the weaker interaction of this support with molybdena.

1. Introduction

Supported molybdenum oxide is one of the most classical and important examples of solid catalysts because of their high activity in industrial processes, such as hydrodesulphurization, hydrodesnitrogenation and hydrodemetallation [1–5]. The activity and selectivity of these systems is deeply modified by their physico-chemical properties, and so these systems, nowadays, receive a lot of attention, in order to assess the effect that preparation conditions, the nature of the support and active phase content have on the properties of the final solids [2, 6–9]. The dispersion and the nature of the active phase are controlled both by the nature of the support (usually another oxide), as well as by the preparation method [10]. So, while molybdena supported on alumina generally contains highly dispersed polymolybdates due to formation of Al–O–Mo linkages, when silica is used as the support the interaction with molybdena is rather low, leading to formation of bulk molybdena [11]. Such a reaction between the support and the supported phase also depends on the load of the latter, and for molybdena/silica systems it has been found that on increasing the molybdenum content, polymolybdates, silicomolybdic acid and molybdena crystallites are formed [12]. On the other hand, the extent of interaction between molybdena and the support is more or less related to the acid-base properties of the surface hydroxyl groups of the support, and it has been claimed that, the fact that silica and molybdena, both being acidic, while alumina is more basic, is the origin of the different ways of the interaction between molybdena and both supports [13].

Although supported metal oxide catalysts are generally prepared by impregnation of the support with aqueous solution of a salt of the supported phase, followed by drying and calcination, it has been shown recently that active catalysts can be also obtained following a dry technique, by mechanically mixing both oxides (the support and the active phase) [14, 15]. So, Margraf *et al.* [16] have shown the formation of highly dispersed molybdena species in MoO_3/Al_2O_3 mixtures, but water vapour is needed to achieve such a dispersion. Leyrer *et al.* [17] have reported that spreading takes place both in the absence and presence of H_2O vapour, while MoO_3 transforms into a surface polymolybdate only in the presence of H_2O vapour. Stampfl *et al.* [11] have

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shown that heating at ~700 K of such mechanical mixtures also leads to a strong interaction between molybdena and alumina, bulk molybdena being undetected after such a treatment.

A study is reported of the effect of the nature of the support, silica or alumina, and the preparation method, impregnation or mechanical mixture, on the dispersion and on the nature of the species existing in catalytic samples formed by molybdena supported on silica or alumina, in order to gain an insight to these materials.

2. Experimental procedure

2.1. Samples preparation

Silica and alumina were from Degussa (Aerosil-200, 0394, and γ-alumina RV0005, respectively), and were calcined overnight at 770 K to eliminate adsorbed organic impurities. MoO_3 was incorporated by impregnating the support with aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, AHM, (Carlo Erba, s.p.a.), leading to samples series I; the solvent was withdrawn by gentle heating at 383 K and the solids thus obtained were calcined in oxygen (30 ml min^{-1}) at 770 or 1100 K for 3 h. All heat treatments were performed in a temperature programmer-controller from RAX (P-C 8601), with a heating rate of 10 K min^{-1}. The relative amounts of AHM and supports were chosen to yield two monolayers of MoO_3 on calcination, as calculated from the specific surface area of the supports calcined at 770 K (see below) and the area covered by a molecule of MoO_3, 15.10^4 pm^2 [18]. Samples belonging to series M were obtained by manually grinding a mixture of the support and MoO_3 (this was obtained by thermal decomposition of AHM in air at 770 K), with the same relative amounts of support and MoO_3 as those of series I. These samples were also calcined, under the same conditions as samples I, at 770 or 1100 K. The former temperature is high enough to achieve decomposition of AHM to MoO_3, and calcination at the last temperature leads to MoO_3 melting on the surface. For comparison purposes, the unloaded supports were also calcined at 1100 K under similar conditions.

2.2. Experimental procedures

Chemical analyses for molybdenum was carried out by atomic absorption (AA) in a ELL-240 Mark 2 instrument. Characterization of the samples was carried out by: (a) X-ray diffraction (XRD), using a Philips 1730 instrument, with CuK_{α_1} ($\lambda = 154.05$ pm) radiation and Ni filters; (b) visible–ultraviolet/diffuse reflectance (V–UV/DR) spectroscopy, in a Shimadzu UV-240 spectrometer provided with a diffuse reflectance accessory and coupled to a Shidmazu PR-1 graphic printer, using a slit of 5 nm and parent support as a reference; (c) infrared spectroscopy (i.r.) in a Perkin-Elmer FTIR-1730 spectrometer using KBr pellets, and the bare support to cancel its absorption bands; (d) nitrogen adsorption measurements at 77 K in a conventional high vacuum pyrex system (residual pressure $\approx 10^{-4}$ N m^{-2}) equipped with a silicon oil vapour diffusion pump, McLeod gauge and grease-free stopcocks, pressure changes being monitored with a MKS pressure transducer; the samples were outgassed *in situ* at 420 K for 2 h before performing the adsorption experiments; (e) temperature programmed reduction (TPR), in a conventional apparatus, with a catharometic detector, using a H_2/Ar (5%) mixture, with a flow of 10 ml min^{-1} and a heating rate of 10 K min^{-1} [19] and without any *in situ* treatment of the samples before carrying out the reduction runs; and (f) transmission electron microscopy (TEM) in a Philips CM-10 microscope, between 40 and 100 kV, using a copper grid, previously impregnated with amorphous carbon, and acetone to suspend the powder.

3. Results and discussion

Chemical analyses for molybdenum, as well as data on the crystallographic phases existing in the samples (according to our XRD results) and specific surface area values, S_{BET}, are shown in Table I.

In the silica-supported samples calcined at 770 K the molybdenum content more or less coincides with the amount expected (26.5% for two monolayers). However, calcination at 1100 K has led to removal by sublimation of MoO_3, decreasing its content to

TABLE I Summary of properties of the samples studied in this work

Sample	Crystallographic phases	Mo[a] (%)	S_{BET}[b]	S_{BET}[c]
S-770	Amorphous	–	205	205
S-1100	Amorphous	–	188	188
A-770	γ-Al_2O_3	–	102	102
A-1100	γ-Al_2O_3	–	102	102
Mo-S-I-770	Amorphous + MoO_3	26.5	97	161
Mo-S-I-1100	Amorphous + MoO_3	1.8	9	9
Mo-S-M-770	Amorphous + MoO_3 (weak)	22.6	120	181
Mo-S-M-1100	Amorphous + MoO_3 (weak)	1.7	12	12
Mo-A-I-770	γ-Al_2O_3 + MoO_3	16.8	58	78
Mo-A-I-1100	γ-Al_2O_3 + MoO_3 + $Al_2(MoO_4)_3$	16.8	54	73
Mo-A-M-770	γ-Al_2O_3 + MoO_3	16.8	77	103
Mo-A-M-1100	γ-Al_2O_3 + MoO_3 + $Al_2(MoO_4)_3$	15.1	49	63

[a] g of Mo/100 g of catalyst; [b] m^2 (g of catalyst)$^{-1}$; [c] m^2 (g of support)$^{-1}$.

ca. 1.8%. On the contrary, most of the molybdenum remains on the surface of alumina (expected value for two monolayers 16.8%) even after calcination at 1100 K. This result indicates that reaction of MoO_3 with alumina probably retains the former on the surface of alumina, avoiding its removal. This conclusion is confirmed from the XRD results: while in the profiles of the silica-supported samples only peaks due to MoO_3 are recorded (silica is amorphous), in the case of the alumina-supported samples, Fig. 1, in addition to peaks of γ-alumina and MoO_3, peaks due to $Al_2(MoO_4)_3$ are recorded in the profiles of samples calcined at 1100 K. On the contrary, only peaks due to γ-alumina and MoO_3 are recorded for samples calcined at 770 K.

From the sharpness of the MoO_3 peaks in the XRD profiles of the samples calcined at 770 K, it can be also concluded that while in the silica-supported sample a larger dispersion of molybdena (lower sized crystallites, with less intense peaks) is achieved by mechanical mixture, the contrary happens in the alumina-supported samples, where a larger molybdena dispersion is achieved by impregnation [20]. Stampfl *et al.* [11] have found that calcination at 720 K for 24 h of molybdena/alumina samples obtained by mechanical mixing leads to cancellation of XRD peaks due to molybdena, because of its dispersion on the alumina surface; in our case, probably because of the large alumina content, the molybdena diffraction peaks are still recorded, Fig. 1. It should be also noted that on calcining at 1100 K, both alumina samples (Mo–A–I–1100 and Mo–A–M–1100) display very similar XRD patterns.

V–UV/DR spectra confirm the presence of the different crystallographic phases, according to the thermal treatment to which the samples have been submitted to. So, for those samples where only MoO_3 exists in addition to the support, the presence of $[MoO_6]$ species is confirmed by two strong absorption bands at 225 and 300 nm, due to $O^{2-} \rightarrow Mo^{6+}$ charge transfer processes, while the presence of tetrahedral $[MoO_4]$ species, as those existing on $Al_2(MoO_4)_3$, is confirmed by a strong absorption band at 275 nm [21–24]. In addition, the intensities of the $[MoO_6]$ bands decreases in the spectra of the silica-supported samples when these are calcined at 1100 K, due to the decrease in its concentration because of removal by sublimation. Praliaud [25] has shown that in molybdena/silica samples obtained by impregnation, reaction of the precursor molybdenum salt and the surface of silica could be expected, leading to $[MoO_6]$ or $[MoO_4]$ species, by incorporation of Mo^{6+} ions into empty reticular holes of the silica framework. Liu *et al.* [20] have indicated that the presence of such tetrahedral species is due to formation of monomeric molybdate species, while the octahedral ones are due to polymeric molybdates. However, due to the large molybdenum content in our samples, it seems that our MoO_3/SiO_2 samples do not contain detectable amounts of $[MoO_4]$ species.

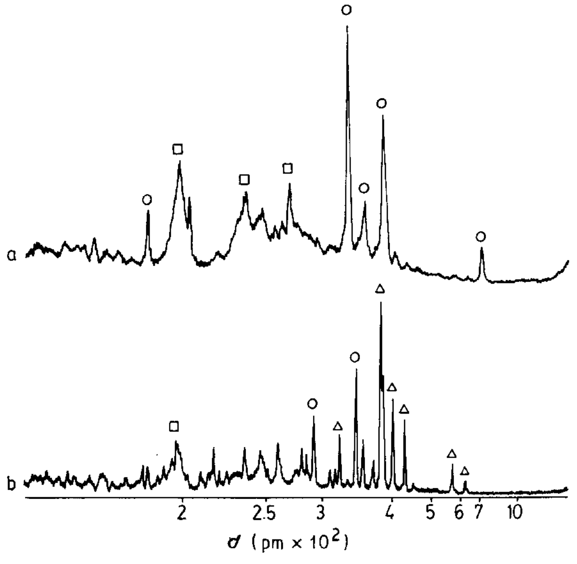

Figure 1 X-Ray diffraction profiles of MoO_3/Al_2O_3 samples prepared by impregnation and calcined at: (a) 770 and (b) 1100 K; (□) peaks due to γ-Al_2O_3; (○) peaks due to MoO_3; (△) peaks due to $Al_2(MoO_4)_3$.

The i.r. spectra of all four samples prepared with alumina are shown in Fig. 2. Only the 1100–800 cm^{-1} range, where the absorption bands due to Mo–O stretching modes are expected, are shown. For sample Mo–A–M–770, where no reaction seems to have taken place, Fig. 2a, a strong absorption band is recorded at 870 cm^{-1}, with two weak shoulders at 920 and 995 cm^{-1}, all three bands due to Mo–O vibrational modes in MoO_3 dispersed (920 cm^{-1}) or in a bulk state (870 and 995 cm^{-1}) [26–28]. However, for sample Mo–A–I–770, where MoO_3 is highly dispersed, the relative intensities of these bands change, and the main band is recorded at 917 cm^{-1} [29]. Finally, both samples calcined at 1100 K show coincident spectra, where the absorption bands have shifted to larger wave numbers, and are originated by the presence of tetrahedral $[MoO_4]$ species [29]. In accordance with the XRD and V–UV/DR results above, the i.r. spectra of the silica-supported samples show only the bands due to bulk MoO_3, although with larger intensities in the spectrum of the sample prepared by impregnation.

Both supports, as well as the samples containing molybdenum, show a complete lack of microporosity, and their nitrogen adsorption curves at 77 K correspond to type II in the IUPAC classification [30], originated by unrestricted monolayer–multilayer adsorption on non-porous or macroporous adsorbents. The specific surface area values, S_{BET}, collected in Table I show an important difference between both sets of samples. With respect to the supports, no change is observed in the S_{BET} value for alumina, while for silica a decrease of $\sim 5\%$ is observed on calcination at 1100 K, although previous studies [31] have shown that such a specific surface area decrease already takes place upon calcination at 973 K for 3 h, and is due to a partial sintering of the silica crystallites. Upon incorporation of molybdenum, however, a general decrease in the specific surface area is observed. For the sake of clarity, we have also shown in Table I the surface area values refering to one gram of support instead of to one gram of solid. With respect to sample

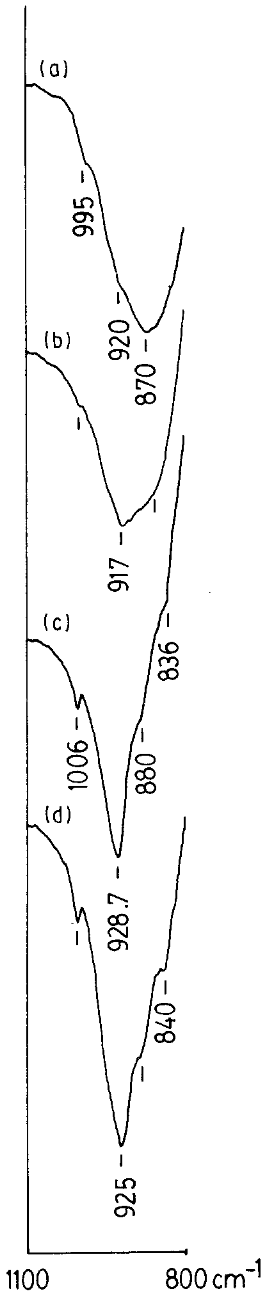

Figure 2 FTIR spectra of samples: (a) Mo–A–M–770; (b) Mo–A–I–770; (c) Mo–A–M–1100, and (d) Mo–A–I–1100.

Mo–A–M–770, the value obtained coincides, within experimental error, with the value corresponding to the unloaded support treated under similar thermal conditions, thus in agreement with previous conclusions about the lack of interaction in this sample between the support and the supported phase. According to previous results [32], the contribution of the MoO_3 particles to the specific surface area can be safely neglected (its specific surface area is only ca. 2–4 $m^2 g^{-1}$). For sample Mo–A–I–770, however, a decrease is observed up to ~78% of the value corresponding to the original support. In this sample, the i.r. results above indicated that some sort of interaction exists between the support and the supported phase, giving rise to a change in the relative intensities of the Mo–O stretching bands. Probably, formation of highly dispersed MoO_3 species on the surface of the alumina particles favours the sintering of the primary particles, but without the creation of micropores, and then decreasing the surface area. When these samples are calcined at 1100 K, both behave similarly, leading to a specific surface area of $51 \pm 3 \, m^2 g^{-1}$, equivalent to $68 \pm 5 \, m^2 (g\,alumina)^{-1}$; melting of MoO_3 and its spreading around the alumina particles makes irrelevant the nature of the primary molybdenum species, leading to sintering of the particles.

The lack of interaction between silica and MoO_3 leads to different results in this series of samples. The fact that the specific surface area of silica decreases as the calcination temperature increases, makes feasible that the surface of silica is not fully stabilized and that it sinters, decreasing its surface area, by prolonged (or repeated) heating even at 770 K. This conclusion seems to be confirmed by the steady decrease in the specific surface area of the silica samples (referred to as one gram of silica) from 205 $m^2 g^{-1}$ for the unloaded support to 188 for the support calcined at 1100 K and to 181 and 161 $m^2 g^{-1}$ for samples Mo–S–F–770 and Mo–S–I–770, respectively. However, on calcining at 1100 K, elimination of molybdena by sublimation takes place together with an extreme sinterization process of the silica crystallites, leading to specific surface area values close to 10 $m^2 g^{-1}$. A similar effect has been previously observed with samples of vanadia supported on this same type of silica [31], where S_{BET} values close to 13 $m^2 g^{-1}$ are obtained for samples heated above the melting temperature of vanadia.

The conclusions reached from the nitrogen adsorption study above, can be confirmed from the transmission electron micrographs for these samples. Bulk MoO_3 is seen as stick-like particles with a length of ~8 μm and a width of ~3–4 μm. All MoO_3/Al_2O_3 samples calcined at 770 K appear as nearly spherical particles with an average diameter of ~20–30 nm, that increases up to 40–50 nm when calcined at 1100 K. Assuming spherical particles and taking into account the specific gravity of γ-alumina (3.5–3.9 $g\,cc^{-1}$), these values would correspond to geometric specific surface area values ~20% lower than the values determined by nitrogen adsorption, indicating that the particles should have some sort of mesoporosity, and even macroporosity, undetectable by nitrogen adsorption. With respect to the silica samples calcined at 770 K, the particles detected by TEM have an average size of ~10–15 nm, that increases up to ~270–280 nm on calcination at 1100 K. This very high increase in the particles size is responsible for the surface area decrease, and it should be noted that in the case of silica samples calcined at 1100 K (Mo–S–I–1100 and Mo–S–M–1100), assuming a specific gravity of 2.2 $g\,cc^{-1}$, the geometric specific surface area would be ~10 $m^2 g^{-1}$, in very good agreement with the value calculated by nitrogen adsorption at 77 K, thus indicating a complete cancellation of mesopores and macropores that could exist in the silica samples heated at 770 K.

The different reactivity of MoO_3 with silica and alumina can be related to the difference in the surface acidity of these three oxides, according to the scale given by Smith [33]. This author has recently proposed a scale of acidity for binary oxides from thermochemical data for oxo acid salts, and, with an arbitrary value of $a = 0.0$ for water, the values of -2.0 (Al_2O_3), 0.9 (SiO_2) and 5.2 (MoO_3) are given; the lower the value, the larger the basicity of the oxide. With this, it can be undoubtedly concluded that reaction of alumina and MoO_3 ($\Delta a = 7.2$) should be very much easier than the reaction between silica and MoO_3 ($\Delta a = 4.3$).

A final approach on the reactivity between MoO_3 and these two supports can be achieved from our TPR studies. The TPR profiles for the samples studied, as well as for bulk MoO_3, are shown in Fig. 3, and some data about these experiments are summarized in Table II. The H_2/Mo ratio values in this table have been calculated assuming that the molybdenum content corresponds to that initially incorporated onto the support, and thus the very low H_2 consumptions for the MoO_3/SiO_2 samples calcined at 1100 K are originated by the low molybdenum content in these two samples (Table I) because of its removal by sublimation as MoO_3. Accordingly, the corresponding TPR profiles (Fig. 3a and b) are nearly flat, and no definitive reduction peak is recorded in any case.

TABLE II Summary of TPR data: hydrogen consumption and positions of the reduction peaks

Sample	H_2/Mo	No. 1	No. 2	No. 3	No. 4
Mo-A-M-770	2.8	765	856	973	1148
Mo-A-I-770	2.6	765	881	998	1148
Mo-A-M-1100	2.3	740	906		
Mo-A-I-1100	2.6	756	923		
MoO_3	3.1		1048(?)		
Mo-S-M-770	3.0	848	963	998	1123
Mo-S-I-770	3.1	873	923	1006	1123
Mo-S-M-1100	0.23	–			
Mo-S-I-1100	0.16	–			

However, curves recorded for all other samples show a series of peaks at different temperatures, and the hydrogen consumptions fit fairly (average $H_2/Mo \approx 2.8$) well with the expected ratio 3.0, within experimental error, unless for sample

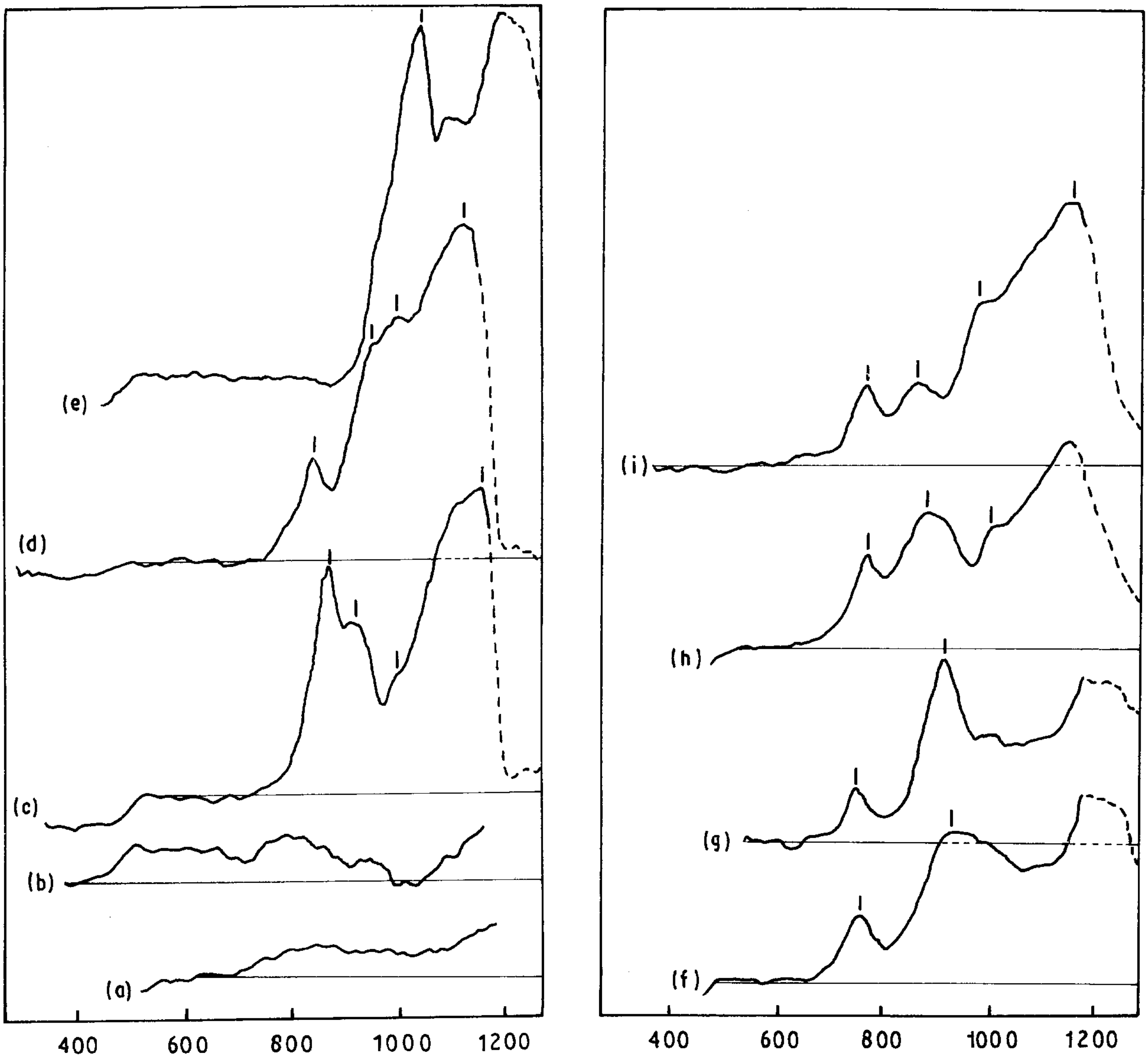

Figure 3 TPR profiles of samples (a) Mo-S-I-1100; (b) Mo-S-M-1100; (c) Mo-S-I-770, (d) Mo-S-M-770; (e) bulk MoO_3; (f) Mo-A-I-1100; (g) Mo-A-M-1100; (h) Mo-A-I-770 and (i) Mo-A-M-770.

Mo–A–M–1100, which chemical analysis data (Table I) already indicated removal of a small fraction of molybdenum.

With respect to bulk molybdena, reduction starts at ≈ 900 K, and the discontinuity observed above this temperature is mainly due to the simultaneous melting of MoO_3 during reduction. With that, the exact position of this reduction maximum is not well defined, and should be somewhere above 1048 K, probably at ~ 1150 K. When MoO_3 is supported either on alumina or silica, its reduction starts at lower temperatures than when unsupported. However, although it could be assumed that the several peaks recorded are due to a step-by-step reduction of molybdenum ions (probably passing from Mo(VI) to Mo(0), through the Mo(IV) and Mo(II) states), this does not seem to be the case, as hydrogen consumptions in everyone of these peaks does not correspond to the amount expected for this step-by-step reduction of Mo(VI) ions to the metallic state. So, it should be concluded that recording several reduction peaks is due to the existence in these samples of Mo(VI) ions with different reducibilities, because of the degree of interaction with the support, and because of a different degree of dispersion, or because formation of new phases.

The behaviour shown by the alumina-supported samples in this study seems to be depending on the calcination temperature and to a lesser extent on the way the supported phase has been incorporated: on calcination at 770 K, the profiles corresponding to samples Mo–A–M–770 and Mo–A–I–770 are rather similar, with four reduction maxima at 765, 869 ± 12, 985 ± 12 (shoulder) and 1148 K, although the relative intensities of these peaks somewhat changes from one sample to another. The maxima at ~770 and that at ~910 K have been ascribed [34] to the reduction of two different types of molybdena. According to Thomas *et al.* [35], reduction starts at a lower temperature when the reducible molybdenum species spreads on the surface of the support; in such a case, the decrease observed in the positions of peak no. 1 from Mo–A samples calcined at 770 to those calcined at 1100 K should be ascribed to a better dispersion of the molybdenum species in the last samples. Peak no. 3 seems to be cancelled in samples Mo–A–1100, but most probably peak no. 2 (at 906–923 K) should correspond to both peaks nos. 2 and 3 of samples calcined at 770 K. That is, formation of $Al_2(MoO_4)_3$ facilitates reducibility of the molybdedum species, although the persistence of a small amount of bulk MoO_3 in this sample (as shown by its XRD profile, Fig. 1b) gives rise to the existence of common reduction peaks in all four samples.

A fairly similar effect is observed with the silica-supported samples calcined at 770 K. Again, several reduction peaks are recorded, that should be ascribed to differently dispersed molybdenum species, but without forming defined species with the support. But, contrary to the findings with the alumina samples, fairly well defined, sharp peaks are recorded in this case, indicating a larger homogeneity of the reducible species. This result agrees with previous reports by Thomas *et al.* [36], indicating that sharper reduction peaks are recorded with bulk materials, while dispersed phases (as in the case of our alumina-supported samples) lead to wider, undefined peaks. The first reduction peak, at 848–873 K, is recorded ~ 80 K above the position for the alumina samples, in agreement with the previously observed poor interaction between silica and MoO_3. The intensity of this first peak is larger for the sample obtained by impregnation; this peak has been ascribed to the reduction of monolayer molybdena and the second one to multilayer–bulk molybdena, as its intensity increases with the molybdenum content [37] and is then recorded very close to that of bulk MoO_3.

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