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A surface dispersion study of silica-supported molybdena

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Surface species formed on MoO_3/SiO_2 catalysts prepared by manually grinding mixtures of both oxides in the presence of water vapour and with molybdenum loadings between 2% and 12% were studied by X-ray diffraction, temperature-programmed reduction and scanning electron microscopy. Polymolybdate species have been identified for molybdenum loadings below 4%, these species condensing to form MoO_3-like phases and orthorhombic MoO_3, as the weight loading increases.

1. Introduction

Catalysts formed by molybdenum oxide supported on alumina or titania are currently attracting a great interest because of their high activity in hydrodesulphurization processes [1, 2] and in selective oxidation of hydrocarbons [3, 4], respectively.

Despite the large number of papers published on these molybdena–alumina and molybdena-titania catalysts, and although silica is also used as a catalyst support in many other reactions, studies carried out on the molybdena–silica system are rather scarce compared to those on MoO_3/Al_2O_3 and MoO_3/TiO_2, especially as this system shows lower catalytic activity in these reactions. However, it has been reported [5, 6] that the MoO_3/SiO_2 system shows good activity levels in alcohol synthesis and also in some photochemical reactions.

Whatever the nature of the support, the catalytic activity of supported molybdena also depends on other factors, such as the dispersion degree and the structure of the supported phase. Therefore, the activity and selectivity have been related to the nature of the active phase, which itself depends on the nature of the support, the molybdena loading and also the preparation method. Although most authors use impregnation of the support with an aqueous molybdate solution, several papers have recently reported the use of mechanical mixtures of the support and molybdena as an alternative route.

With regards to the MoO_3/SiO_2 system, Louis *et al.* have reported [7] that the dispersion of molybdena in this system is of paramount importance in determining the ability of the catalyst to produce O^- ions and on the catalytic behaviour in methanol oxidation [8] or in photo-induced methathesis processes [9].

Smith *et al.* [10] have recently reported the effect of the nature of surface species on the activity and selectivity of MoO_3/SiO_2 catalysts for the partial oxidation of methane to formaldehyde. According to these authors, a highly dispersed silicomolybdic species with terminal $Mo=O$ sites exists for low MoO_3 loadings; as the molybdenum content is increased, these sites are transformed into polymolybdate species, forming Mo–O–Mo bridging sites at the expense of $Mo=O$ sites. Finally, crystalline MoO_3 is detected at high molybdenum contents.

Stencel *et al.* [11] have investigated the surface structure of SiO_2-supported Mo(VI) as a function of molybdenum loading, the impregnation technique used to incorporate molybdenum, and hydration–calcination cycles. Different surface molybdenum species have been found, depending on the molybdenum loading. Using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, Kakuta *et al.* [12] have also found different types of molybdenum oxides in addition to MoO_3 for high loadings, and species different from heptamolybdate for low loadings.

With regard to samples prepared by mechanically mixing molybdena and silica, Leyrer *et al.* [13] have reported the exclusive presence of MoO_3, according to the Raman spectra of MoO_3–SiO_2 samples containing $\approx 8\%$ and calcined in the presence of water vapour.

In the present work, the dispersion and nature of the species formed in MoO_3–SiO_2 samples prepared by calcination of mechanical mixtures in the presence of water vapour have been analysed by X-ray diffraction (XRD) and temperature-programmed reduction (TPR); scanning electron microscopy (SEM) of the samples was also carried out. With this, the overall

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effect of the nature of the support on the surface species of supported molybdena was ascertained fully by investigating a more acid support.

2. Experimental procedure

2.1. Sample preparation

The support was SiO_2 (Aerosil, Degussa, Germany) and was calcined in air overnight at 770 K to eliminate adsorbed organic impurities. MoO_3 was prepared by thermal decomposition of $(NH_4)_6Mo_7O_{24}.4H_2O$ (AHM, Carlo Erba) at 770 K in air for 5 h.

The physical mixtures were prepared by manually grinding MoO_3 and SiO_2, in different relative amounts, in an agate mortar for 20 min. These samples were calcined at 770 K for different periods of time (2, 24 and 100 h) in a static, uncontrolled atmosphere in an open crucible. Chemical analysis after calcination indicated no loss of molybdenum.

Naming of the samples, according to the molybdenum content, has been summarized in Table I. Samples are designated nMS-T, $n = \%$ of molybdenum, M = MoO_3, S = SiO_2 and T = calcination time.

2.2. Techniques

X-ray diffraction (XRD) patterns were recorded on a Siemens-500 diffractometer using CuK_{α_1} radiation ($\lambda = 154.05$ pm) with a graphite monochromator and interfaced to a DACO-MP data acquisition microprocessor provided with Difract/AT software. Temperature-programmed reduction (TPR) profiles were recorded in a conventional apparatus with a catharometric detector, using a 5% H_2/Ar mixture as carrier gas, with a flow of 50 ml min^{-1} and a heating rate of 10 K min^{-1}. Good resolution of the different reduction steps under these experimental conditions was ensured by using sample weights containing ~ 100 μmol MoO_3 [14]. SEM images of samples were obtained with a digital scanning microscope Zeiss DSM 940 between 20 and 30 kV. Maximum resolution was 5 nm at 30 kV. Samples were metallized with gold during 150 s using a BIO-RAD-SEM loading, working at 1.6 kV and 25 mA.

TABLE I

Sample	Calcination time (h)	Mo(%)	H_2/Mo
Bulk MoO_3			3.1
2MS-2	2	2	nm[a]
4MS-2	2	4	nm
6MS-2	2	6	nm
8MS-2	2	8	nm
10MS-2	2	10	nm
12MS-2	2	12	nm
2MS-24	24	2	2.4
4MS-24	24	4	2.4
6MS-24	24	6	2.8
8MS-24	24	8	3.3
10MS-24	24	10	2.8
12MS-24	24	12	2.6
2MS-100	100	2	2.3
4MS-100	100	4	2.4
6MS-100	100	6	2.9
8MS-100	100	8	3.5
10MS-100	100	10	3.2
12MS-100	100	12	2.9

nm = not measured.

3. Results and discussion

3.1. X-ray diffraction

The dispersion of the supported phase has been studied by XRD following the variation in the integrated intensity of the MoO_3 relevant peaks at 381 pm due to planes (1 1 0), 346 pm due to planes (0 4 0), and 326 pm due to planes (0 2 1).

The XRD patterns of the calcined catalysts, Fig. 1, are similar to that of MoO_3, but the integrated intensities are lower than those for the reference materials, a physical mixture of MoO_3 and SiO_2 with the same molar ratio, but not submitted to any calcination treatment.

No diffraction peak due to MoO_3 was recorded in the XRD profiles of samples containing up to 4% Mo, despite these peaks being easily recorded in the reference samples. For larger molybdenum contents, however, the integrated intensities are lower than for the reference materials containing the same concentration of molybdenum. This weakening should be attributed either to the presence of small MoO_3 particles with sizes undetectable by XRD or to the formation of highly dispersed surface species, like silicomolybdate and polymolybdate [4, 15–17].

A comparison of the dispersion degree of molybdena in the different samples can be roughly carried

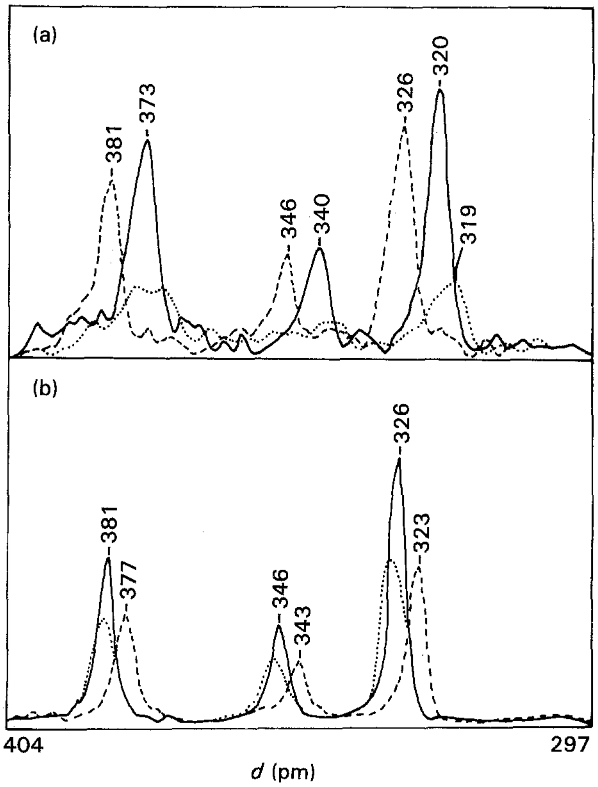

Figure 1 X-ray diffraction profiles of samples (a) 6MS and (b) 12MS calcined at 770 K for (——) 2 h, (– – –) 24 h, (...) 100 h.

out from the integrated intensities of the diffraction peaks of MoO_3. The XRD profiles of samples 6MS and 12MS submitted to calcination for 2, 24 and 100 h are shown in Fig. 1. In the case of sample 6MS-100, the peaks are very weak, and almost indistinguishable from the signals due to noise. The integrated intensities of the peaks due to samples 6MS-2 and 6MS-100 are only 25% and 10%, respectively, of the values for the corresponding uncalcined reference materials; in other words, 75% and 90%, respectively, of molybdena, is in the amorphous state in these two samples after the thermal treatment.

When the molybdena content is increased, however, the integrated intensities of these peaks are larger, but this should be due not to a lower dispersion degree, but to the fact that larger amounts of MoO_3 are present, and, although the absolute amount of molybdena dispersed could be identical in both sets of samples, the relative dispersion will be obviously lower in the case of the 12MS samples.

The positions and linewidths of the MoO_3 peaks in the profiles recorded for samples 6MS-24 and 6MS-100 do not exactly coincide with those of bulk MoO_3. This is not an instrumental artifact, as the XRD profile has been recorded using aluminium sample holders, and thus using aluminium as an internal reference. A similar behaviour has been reported by Ismael *et al.* [18] in the XRD profiles of silica-supported molybdena samples prepared using different impregnation techniques. These authors ascribe these variations to the presence of MoO_3 or MoO_3-like phases. This may be attributed to the existence of different MoO_3-like phases with minor distortion from well-crystallized orthorhombic MoO_3 crystallites.

3.2. Scanning electron microscopy

Fig. 2 shows scanning electron micrographs of parent SiO_2 and of samples 6MS-24, 12MS-24 and 12MS-100. Silica is composed of aggregates formed by very small particles, Fig. 2a. However, crystalline species, probably due to MoO_3, are detected in the other samples. These species appears as long platelets, well isolated or gathered as aggregates in the case of 12MS

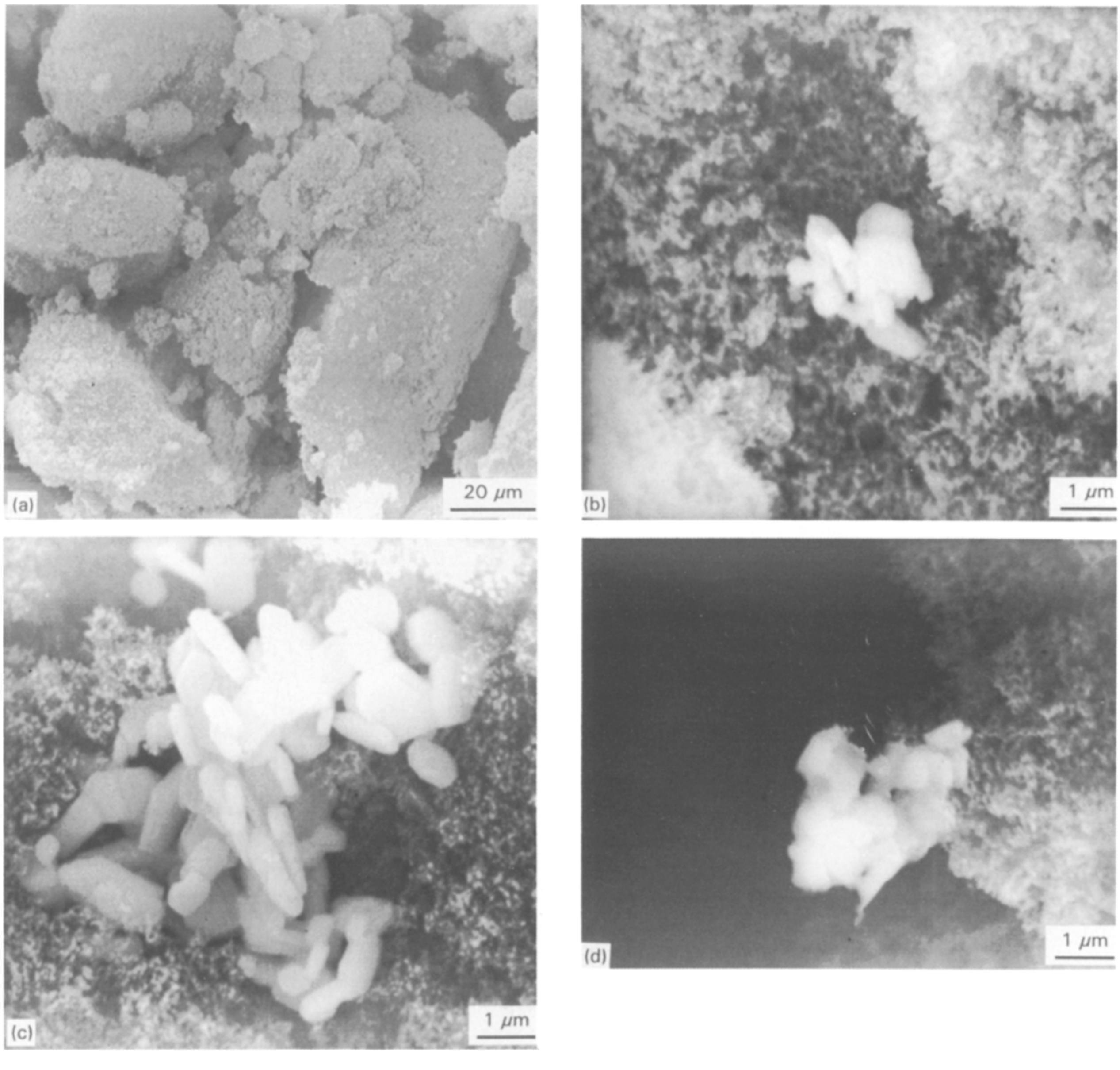

Figure 2 Scanning electron micrographs of (a) SiO_2 support, (b) sample 6MS-24, (c) sample 12MS-24, and (d) sample 12MS-100.

sample. The morphology of these particles coincides with that reported for bulk molybdena.

As the calcination time is increased, a loss of the regular particle shape is detected as the particles seem to aggregate, forming a conglomerate. This behaviour is clearly detected in sample 12MS-100, and is in agreement with the slight broadening of the peak at 326 pm in the XRD pattern with respect to the same XRD peak in sample 12MS-24. A similar effect is observed in sample 6MS, although in this case it happens even with a shorter calcination period.

The micrographs corresponding to sample 6MS-100 are coincident with that of SiO_2; MoO_3 particles could not be detected after mapping of the sample at different zones because of the low concentration of crystalline MoO_3 as detected by XRD.

3.3. Temperature-programmed reduction

The TPR profiles for samples calcined for 24 and 100 h are shown in Figs 3 and 4. The profile for bulk MoO_3 is also shown. The molar H_2/Mo ratios, as calculated from the molybdenum content in the samples and hydrogen consumption, are given in Table I.

Temperature-programmed reduction of bulk molybdena (see inset Fig. 3) starts at 825 K with a total hydrogen uptake of 3.1 H_2/Mo, corresponding to the total reduction of Mo^{6+} ions to Mo^0. When molybdena is supported on silica, significant differences were observed in the corresponding TPR profiles when varying the molybdenum content, suggesting changes in the nature and distribution of the molybdenum species on the surface of the catalysts. Some of these TPR-monitored changes were, however, undetected by XRD.

Hydrogen consumptions lower than expected (≈ 2.4) are recorded in some of the low-loaded samples, but in these cases the TPR profile has not recovered the baseline at the highest temperature attainable by our experimental system.

As shown in Figs 3 and 4, reduction in all silica-supported samples starts at temperatures ~ 250 K

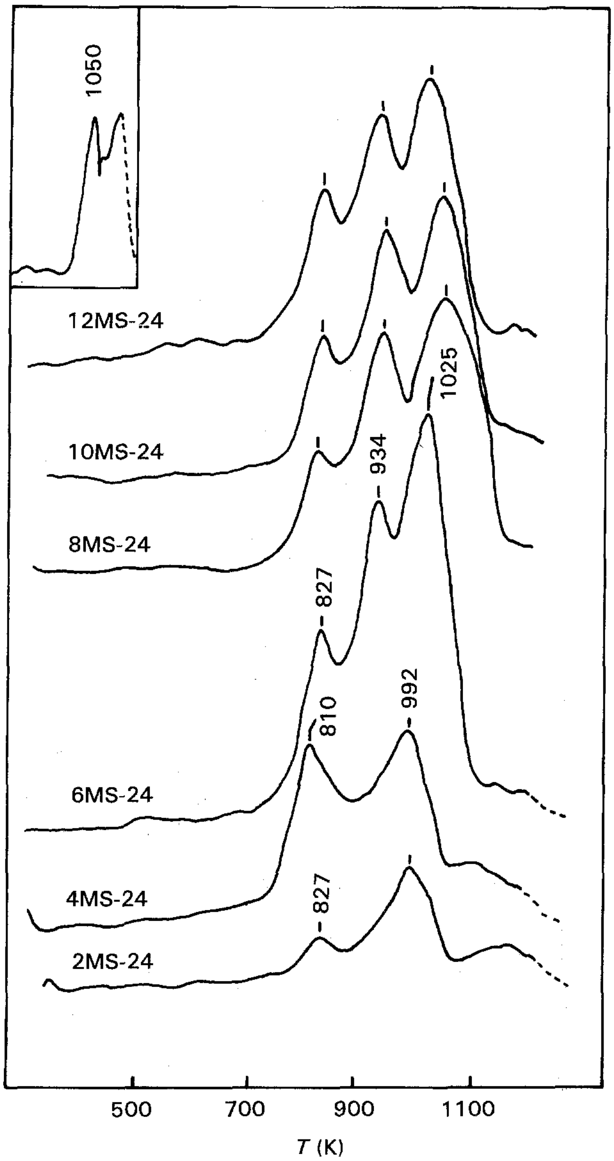

Figure 3 Temperature-programmed reduction profiles of samples calcined for 24 h. Inset: reduction profile of bulk MoO_3.

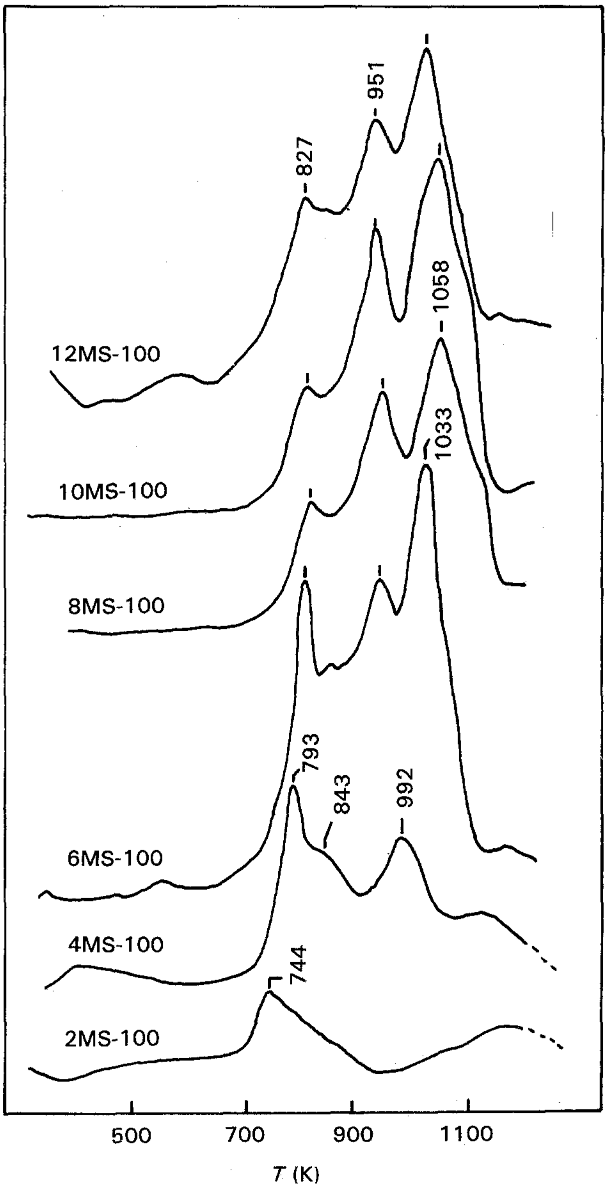

Figure 4 Temperature-programmed reduction profiles of samples calcined for 100 h.

below that needed to begin reduction of bulk molybdena, thus suggesting the presence of well-dispersed molybdenum-containing species, that are more easily reduced than bulk molybdena.

At a first glance, samples with molybdenum contents above 6%–8% give rise to TPR curves with three maxima, and only one (sample 2MS-100) or two (sample 2MS-24) maxima are recorded for lower molybdenum contents.

For sample 2MS-24, where, according to the XRD data, molybdena is fairly well dispersed, two reduction maxima are recorded at 827 and 992 K, Fig. 3. Because no molybdena peak due to orthorhombic MoO_3 is recorded in the XRD pattern of this sample, the two reduction maxima should be ascribed to small MoO_3-like particles; recording of two different peaks can be tentatively ascribed to reduction of particles which may differ in their crystalline size.

Increase of the calcination time modifies the reduction profile, and thus, only a new form reducing at 744 K is developed in sample 2MS-100. This suggests that new molybdenum species are formed on calcining for 100 h, as only a single peak is recorded, and it appears ~ 100 K earlier than the first reduction feature of sample 2MS-24. This species should be ascribed to polymolybdates, because the reduction maximum (744 K) is recorded in a position fairly close to that for reduction of polymolybdate species in MoO_3/Al_2O_3 samples prepared by mechanical mixtures [19], and also in Al_2O_3-supported molybdena samples prepared by impregnation [20].

Formation of polymolybdate species in MoO_3/Al_2O_3 and MoO_3/TiO_2 samples prepared by mechanical mixing and calcined in the presence of water vapour has been explained on the basis of the formation of a Mo(VI) oxyhydroxide, $MoO_2(OH)_2$ [21]. However, the formation of such species in samples MoO_3/SiO_2 seems to be unlikely, due to the lack of reaction in the solid state between MoO_3 and SiO_2 [13]. Stencel *et al.* [11] have studied MoO_3/SiO_2 samples prepared by impregnation and submitted to successive cycles of exposure to water vapour and calcination in oxygen; these authors have reported the formation of crystalline MoO_3, highly dispersed molybdate species and silicomolybdic acid, depending upon molybdenum loading; in particular, in samples with 4% molybdenum they report the formation of silicomolybdic acid which is destroyed by calcination in oxygen at 770 K and then it is subsequently restored during rehydration.

Recently, Smith *et al.* [10] have studied by Raman spectroscopy and TPR the effect of molybdenum loading on the nature of the surface species formed in MoO_3/SiO_2 samples prepared by wet impregnation and calcined at 950 K. Their studies suggest the presence of three different species on these samples: at low loading levels (less than 2% molybdenum by weight) the dominant structure corresponds to silicomolybdic species. As loading levels increase, surface-coordinated polymeric molybdate species begin to form, and at loading levels above 3.5%, crystalline MoO_3 is easily detected by Raman spectroscopy through its characteristic bands at 818 and 995 cm^{-1}.

The reduction profile of sample 4MS-24 is similar to that for sample 2MS-24, although the relative intensity of the low-temperature peak at 810 K is markedly increased, and separation between both peaks is not as clear as in sample 2MS-24, thus suggesting that a third, weak reduction effect should exist at intermediate temperatures. In the case of sample 4MS-100, the first peak has markedly increased its intensity, and a shoulder at 843 K is clearly recorded, while the integrated intensity of the peak at 992 K seems to be lower than that observed in sample 4MS-24.

When the molybdenum content is increased to 6% and higher values, the reduction profiles are very similar, thus suggesting that the same species exist in all these samples. Even the relative intensities of the three peaks recorded are fairly coincident. The species responsible for these reduction maxima should correspond to MoO_3 particles. From EXAFS spectroscopy studies, Kakuta *et al.* [12] have reported the existence of crystalline MoO_3 in silica-supported MoO_3 samples prepared by impregnation and with a molybdenum content higher than 5%. According to these authors, for these fairly large loadings, molybdena clusters with different particle sizes are formed.

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References

1. H. F. LIU, R. S. LIU, K. Y. LIEW, R. E. JOHNSON and L. H. LUNSFORD, *J. Am. Chem. Soc.* **106** (1982) 4117.
2. J. ABART, E. DELGADO, G. ESST, H. JEZIOROWSKI, H. KNÖZINGER, N. THIELE, X. A. H. WANG and E. TAGLAUER, *Appl. Catal.* **2** (1981) 155.
3. T. ONO, Y. NAKAGAWA, H. MIYATA and K. KUBOKAWA, *Bull. Chem. Soc. Jpn* **57** (1984) 1025.
4. Y. C. LIUM, G. L. GRIFFIN, S. S. CHAN and I. E. WACHS, *J. Catal.* **94** (1985) 108.
5. A. OGATA, A. KAZUSAKA and M. ENYO, *J. Phys. Chem.* **90** (1986) 5201.
6. T. YANG and J. LUNSFORD, *J. Catal.* **103** (1987) 55.
7. C. LOUIS, L. MARCHESE, S. COLUCCIA and A. ZECCHINA, *J. Chem. Soc. Farad. Trans. I* **85** (1989) 1655.
8. M. CHE, C. LOUIS and J. M. TATIBOUET, *Polyhedron* **5** (1986) 123.
9. M. ANPO, M. KONDO, Y. KUBOKAWA, C. LOUIS and M. CHE, *J. Chem. Soc. Farad. Trans. I* **84** (1988) 2771.
10. M. R. SMITH, L. ZHANG, S. A. DRISCOLL and U. S. OZKAN, *Catal. Lett.* **19** (1993) 1.
11. J. M. STENCEL, J. R. DIEHL, J. R. D'ESTE, L. E. MAKOVSKY, L. RODRIGO, K. MARCINKOWSKA, A. ADNOT, P. C. ROBERGE and S. KALIAGUINE, *J. Phys. Chem.* **90** (1986) 4739.
12. N. KAKUTA, K. TOHJI and Y. UDAGAWA, *ibid.* **92** (1988) 2583.
13. J. LEYRER, R. MARGRAF, E. TAGLAUER and H. KNÖZINGER, *Surface Sci.* **201** (1988) 603.
14. P. MALET and A. CABALLERO, *J. Chem. Soc. Farad. Trans. I* **84** (1988) 2369.
15. A. CASTELLAN, J. C. J. BART, A. VAGHI and N. GIORDANO, *J. Catal.* **42** (1976) 162.

16. P. GAJARDO, D. PIROTTE, P. GRANGE and B. DELMON, *J. Phys. Chem.* **83** (1979) 1780.
17. P. GAJARDO, P. GRANGE and B. DELMON, *ibid.* **83** (1979) 1771.
18. H. M. ISMAIL, C. R. THEOCHARIS and M. I. ZAKI, *J. Chem. Soc. Farad. Trans. I* **83** (1987) 2835.
19. M. DEL ARCO, S. R. G. CARRAZAN, V. RIVES, F. J. GIL LLAMBIAS and P. MALET, *J. Catal.* **141** (1993) 48.
20. M. DEL ARCO, S. R. G. CARRAZAN, C. MARTIN, I. MARTIN, V. RIVES and P. MALET, *J. Mater. Chem.*, **3** (1993) 1313.
21. O. GLEMSER and H. G. WENDLANDT, *Adv. Inorg. Chem. Radiochem.* **5** (1963) 215.

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