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Reactivity of MoO_3: effect of molybdenum with Al_2O_3 precursor and the presence of water vapour on the dispersion of the surface phases

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MoO_3/Al_2O_3 systems have been prepared by calcining at 770 K alumina impregnated with ammonium heptamolybdate (aq), or by calcining molybdena/alumina mixtures at 770 K. Surface polymolybdates have been observed by laser Raman spectroscopy in samples prepared by impregnation: for calcined MoO_3/Al_2O_3 mixtures, X-ray diffraction indicates MoO_3 readily spreading over the alumina surface in the presence of water vapour, and this being almost complete after calcination for 2 h.

1. Introduction

Supported oxides are extremely important materials because of their applications as catalysts [1, 2]; for example, MoO_3/Al_2O_3 is the precursor material for hydrotreatment catalysts [3–7].

The so-called "monolayer-type" catalysts are formed when a high dispersion degree of the active component is achieved on the surface of a support, and it is assumed that the supported phase exists as a monolayer on the support surface. However, catalytic properties are not only determined by the high dispersion degree, but also by the structure of the resulting active phase. The dispersion and the nature of the supported active oxide phase are usually determined by the nature of the support oxide and the preparation method [8, 9].

One sort of catalysts is usually prepared by impregnation of the support with an aqueous solution of ammonium heptamolybdate. It is now well established that upon calcination (which decomposes the polymolybdate ion), the molybdenum species in these catalysts exist as a surface polymolybdate, which has been considered a necessary precursor state for highly active MoO_3/Al_2O_3 catalysts [10, 11].

However, it has been shown recently that dispersed supported oxide catalysts can also be obtained from physical mixtures of both oxides (support and supported phase) by spreading the active phase under "dry conditions" on the surface of the support oxide during thermal treatment [12–14].

Xie *et al.* [12] showed that after heating in air for 24 h a mixture of MoO_3 and Al_2O_3 (where the MoO_3 content does not exceed the monolayer capacity) the characteristic X-ray diffraction peaks of MoO_3 are no longer recorded. This led these authors to conclude that MoO_3 could disperse spontaneously on to the surface of Al_2O_3 as a monolayer when these oxides were mixed and heated at a temperature below their melting points.

Stampfl *et al.* [8] studied the calcination of MoO_3 on various oxides at 770 K in air for 24 h and also reported the absence of bulk MoO_3 peaks in the Raman spectra. Margraf *et al.* [15] reported that the formation of highly dispersed molybdena species on MoO_3/Al_2O_3 mixtures takes place exclusively in the presence of water vapour. In a recent paper, the authors [16], using ion-scattering spectroscopy, have shown that spreading of molybdenum species occurs during calcination of physical mixtures in flowing oxygen, in the absence and in the presence of water vapour.

In the present work, our interest has been focused on the role that the composition, method of preparation and calcination (in either dry or moist oxygen streams) play on the spreading and surface compound formation in MoO_3/Al_2O_3 systems. The dispersion of MoO_3 on Al_2O_3 in these samples was studied by X-ray diffraction (XRD) and surface compound formation was analysed by laser Raman spectroscopy (LRS).

2. Experimental procedure

2.1. Materials and sample preparation

The Al_2O_3 support (γ-alumina, Degussa RV005) was calcined overnight at 770 K to eliminate adsorbed organic impurities. Alumina was impregnated with an aqueous solution of $(NH_4)_2Mo_7O_{24}\cdot 4H_2O$ (AHM) to

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obtain a slurry. This was magnetically stirred to homogenize it and then was dried overnight at 383 K. The samples were finally calcined at 770 K in a static air atmosphere in an open crucible in the oven for 2 h.

Three other sets of samples were prepared by manually grinding the support and MoO_3 (this was previously obtained by thermal decomposition of AHM in air at 770 K) in an agate mortar for 20 min. These physical mixtures were calcined at 770 K in three different ways: in a quartz reactor under an oxygen (99.95%) flow (30 ml/min^{-1}), either dry or with water vapour (partial pressure ~ 5.6 $kN\,m^{-2}$), and in a static atmosphere, as described above, for samples prepared by impregnation.

In all cases, the relative amounts of AHM (or MoO_3) and Al_2O_3 were chosen to yield 0.4, 0.7 or one monolayer of MoO_3 upon calcination, as calculated from the specific surface area of the support calcined at 770 K (105 $m^2\,g^{-1}$) and the area covered by one molecule of MoO_3, 15×10^4 pm^2 [17]; that is, in this case we speak of a "geometrical monolayer" [18]. With this, one monolayer equals 16.81 g MoO_3/100 g Al_2O_3.

Naming of the samples, according to the molybdenum loading and to the preparation method, is summarized in Table I.

2.2. Experimental techniques

XRD diffraction patterns were recorded on a Siemens-500 diffractometer using $CuK_{\alpha1}$ radiation ($\lambda = 154.05$ pm) with a nickel filter and interfaced to a DACO-MP data acquisition microprocessor.

Visible–ultraviolet spectra were obtained by the diffuse reflectance technique (V–UV/DR) in a Shimadzu UV-240 spectrometer fitted with a diffuse reflectance accessory and coupled to a Shimadzu PR-1 graphic printer, using a slit of 5 nm and MgO or parent Al_2O_3 as reference.

Laser Raman spectra were recorded in the wave number range 400–1200 cm^{-1} using a computer-controlled Jobin Yvon spectrometer (U-100 model). The 514.5 nm line of an argon ion laser (Spectra Physics, model 165) was used for excitation and a laser power of 20 mW at the sample was applied. The wave number accuracy was 4 cm^{-1}.

Specific surface area values were determined by nitrogen adsorption at 77 K, using a Flowsorb 2300A apparatus from Micromeritics; the samples were degassed *in situ* at 420 K for 1 h prior to carrying out the measurements.

3. Results and discussion

3.1. Impregnation

All samples prepared via impregnation had specific surface areas amounting to 90% of the value determined for the unloaded support.

The role of the molybdenum content and the preparation method on the dispersion of the supported active phase has been studied by XRD from the area of MoO_3 relevant peaks at 381 pm (1 1 0), 346 pm (0 4 0) and 326 pm (0 2 1), in the XRD pattern.

Fig. 1 shows the XRD patterns of a series of MoO_3/Al_2O_3 samples, in the range 300–750 pm (where diffraction peaks due to MoO_3 are expected to be recorded) prepared by impregnation. While peaks due to crystalline MoO_3 are recorded for Sample I-1, a marked decrease in the intensities of these MoO_3 peaks is observed for Sample I-0.7, and in Sample I-0.4, no MoO_3 peak is detected. It should be stressed that the disappearance of MoO_3 peaks is not due to the detection limit of the X-ray diffractometer, because in samples containing 1% MoO_3 by weight (equivalent to less than 0.1 monolayer), prepared by mechanical mixtures, but uncalcined, sharp MoO_3 peaks are recorded. Therefore, the disappearance of XRD peaks originated by MoO_3 should be attributed either to an improved MoO_3 dispersion or to the formation of surface molybdate–polymolybdate species on the surface of the support (see below).

These results are in close agreement with those obtained from mechanical mixtures submitted to calcination at 770 K for longer periods of time (24 h) than those used in the present work [19]. In these samples calcined for 24 h, formation of bulk MoO_3 (in addition to the monolayer) is achieved when the amount of MoO_3 is more than 0.72 theoretical monolayers, the species present in these systems being similar to those

TABLE I Summary of preparation conditions of the samples

Sample	Preparation method	Mo loading[a]	Calcination conditions
I-0	Impregnation	0.4	Open air
I-0.7	Impregnation	0.7	Open air
I-1	Impregnation	1	Open air
MD-0.4	Mechanical mixture	0.4	Dry oxygen
MD-0.7	Mechanical mixture	0.7	Dry oxygen
MD-1	Mechanical mixture	1	Dry oxygen
MW-0.4	Mechanical mixture	0.4	Wet oxygen
MW-0.7	Mechanical mixture	0.7	Wet oxygen
MW-1	Mechanical mixture	1	Wet oxygen
MO-0.4	Mechanical mixture	0.4	Open air
MO-0.7	Mechanical mixture	0.7	Open air
MO-1	Mechanical mixture	1	Open air

[a] As MoO_3 monolayers.

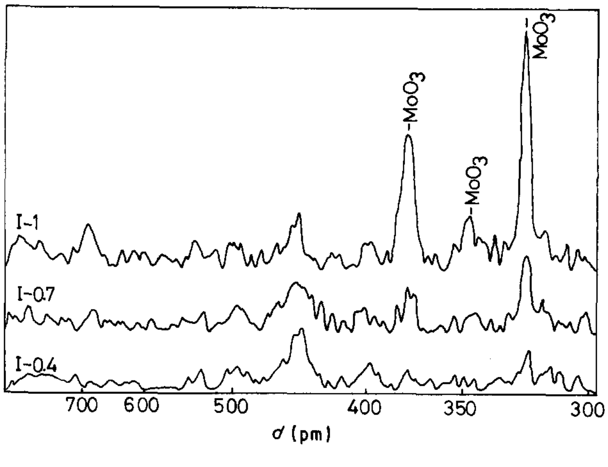

Figure 1 XRD patterns for Samples I-0.4, I-0.7 and I-1.

obtained by the impregnation method. In other words, although with an amount of MoO_3 equivalent to 0.72 monolayers a complete monolayer should not be formed, with contents larger than 0.72 monolayers bulk MoO_3 is already detected.

The Raman spectra of Samples I-0.4 and I-0.7 are shown in Fig. 2. The spectrum for Sample I-0.7 shows characteristic MoO_3 bands at 991, 816 and 662 cm^{-1}, while in the spectrum recorded for Sample I-04, two bands at 950 and 970 cm^{-1}, related to the existence of surface polymolybdate [17], can be detected in addition to the MoO_3 features at 991 and 816 cm^{-1}. The band at 950 cm^{-1} in MoO_3/A_2O_3 samples has been ascribed by Payen *et al.* [20] to polymolybdate species when the laser power is $\sim$ 20 mW, i.e. under experimental conditions similar to those used in this work. On the other hand, the Raman spectrum recorded for $Mo_7O_{24}^{6-}$ species in solution at pH = 3.9 shows two bands at 901 and 945 cm^{-1} [21], ascribed to stretching modes of Mo=O bonds. These bands shift to higher wave numbers, 906 and 951 cm^{-1}, respectively, when such species are bound to the alumina surface (wet catalyst), and, on calcination, the band at 951 cm^{-1} splits into two bands at 950 and 970 cm^{-1}.

The fact that the spectra for Samples I-0.7 and I-1 clearly show the characteristic bands of MoO_3 does not necessarily exclude the presence of polymolybdate species. According to the X-ray diffraction results, the amount of bulk MoO_3 seems to decrease and even disappear upon calcination, contrary to the data found by using Raman spectroscopy, but it may be due to the fact that Raman spectroscopy should be less sensitive to the bulk of the crystallites than to the surface layers, due to the use of longer wavelength radiation than in X-ray diffraction. Raman sensitivity has been shown by Chan *et al.* [22] in WO_3/Al_2O_3 catalysts, their results showing that the Raman intensity of bulk WO_3 is 160 times that of surface tungsten oxide phases.

V–UV/DR spectra for these samples are shown in Fig. 3. On decreasing the molybdenum concentration the intensity of the band at 240 nm, usually ascribed to monomeric tetrahedral MoO_4^{2-} species [4], increases and, in addition, a decrease in the intensity of the band at 300 nm, ascribed to octahedral polymolybdate or MoO_3, is observed. This might be due to a transformation of octahedrally coordinated molybdenum species, Mo(O), into tetrahedrally coordinated ones, Mo(T), although the simultaneous presence of octahedral species cannot be excluded because Mo(O) species also give rise to bands at 240 nm. In addition, it has been recently claimed [23, 24] that the use of the 300 or 240 nm bands to distinguish between Mo(O) and Mo(T) species should be reconsidered, as other effects, such as the condensation of Mo(O) units, may have a stronger effect in the HOMO–LUMO gap than such a Mo(O)/Mo(T) transformation, thus probably accounting for the shift in the positions of the bands. Our results reported here are in agreement with such an idea, as the increase in the intensity of the band at 240 nm for Sample I-0.4 cannot be exclusively (or even partially) due to the formation of new Mo(T) species, because the band due to the M=O stretching mode in such MoO_4^{2-} species at 920 cm^{-1} [20] is not recorded (Fig. 2). Similar results have been drawn from the V–UV/DR spectra of solid AHM and of AHM supported on Al_2O_3, calcined at 770 K [21].

3.2. Mechanical mixtures

For the samples obtained by impregnation and calcined at 770 K, all those prepared by the mechanical mixing of both oxides also had specific surface areas amounting to 90% of the value determined for the unloaded support. In both series of samples, this fact might be attributed to the formation of highly dispersed MoO_3 species on the surface of the alumina particles (see below) which favour the sintering of the

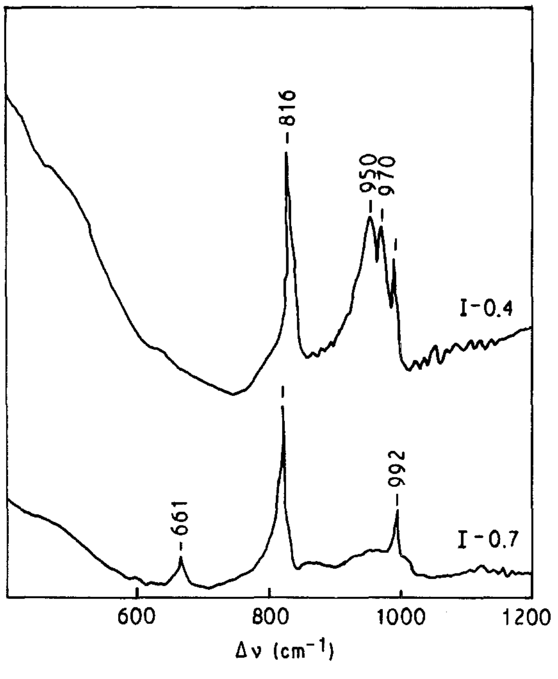

Figure 2 Raman spectra of Samples I-0.4 and I-0.7.

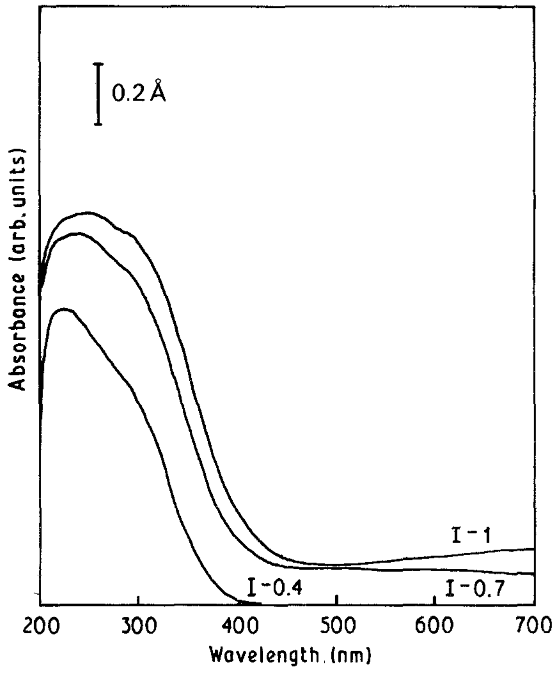

Figure 3 V–UV/DR spectra for Samples I-0.4, I-0.7 and I-1.

primary particles, but without generation of micropores.

The different dispersion capacities of the MoO_3–Al_2O_3 system, either in a dry oxygen flow or with water vapour, has been shown by XRD. The experimental dispersion capacity was calculated from the residual amount of crystalline MoO_3, as calculated from the area of the peak at 329 pm in the XRD patterns, after the mixtures of MoO_3 and Al_2O_3 had been calcined at 770 K for 2 h. Table II lists the experimental dispersion capacities (g MoO_3 "disappeared" or reacted by 100 g Al_2O_3) and the dispersion percentage (calculated from the initial amounts of MoO_3 by 100 g Al_2O_3 in each sample) for MO, MW and MD series of samples. From these data, it is clear that for samples MW-0.4 and MO-0.4 the dispersion of the MoO_3 phase (70%–80%) is very much larger than for sample MD-0.4 (40%). The present results undoubtedly demonstrate that dispersion can also take place in the absence of water vapour (sample MD-0.4), but its presence does favour the dispersion for even relatively low heating periods [16].

For samples containing 0.7 monolayers of MoO_3 (i.e. 0.7 "geometrical" monolayers, but approaching the real monolayer value, 0.72), again the dispersion reached for samples prepared in the presence of water vapour (series MW or MO) is larger than for samples prepared in dry oxygen (series MD). Similar results are obtained for samples with one monolayer.

The results obtained for these systems clearly show that on heating samples with 0.4 monolayers (even for only 2 h) in an oxygen flow in the presence of water vapour or in a certain uncontrolled vapour pressure in an open-air oven, a high dispersion percentage of molybdenum is attained, this percentage being roughly twice that found when the calcination occurs in the absence of water vapour.

A similar behaviour is found in samples containing 0.7 monolayers, indicating that a double amount of MoO_3 has been dispersed on the Al_2O_3 surface. However, samples with one monolayer show the same dispersion capacity as the systems with 0.7 monolayers; so it is evident that the support surface had already been practically covered by molybdenum-containing species when the amount of MoO_3 is 0.7 monolayers and the calcination time is 2 h. The total amount of MoO_3 dispersed in samples with 0.7 or 1 monolayers is the same in all four samples prepared in the presence of water vapour (10.1 ± 0.1 g/100 g Al_2O_3), and is the same also in both samples prepared in dry oxygen (6.15 ± 0.15 g/100 g Al_2O_3).

TABLE II Analysis of MoO_3 dispersion on the surface of alumina, depending on the preparation method

Sample	Initial[a]	Disappeared[b]	Dispersion (%)[c]
MO-0.4	6.72	4.7	70
MO-0.7	11.72	10.0	85
MO-1	16.81	10.0	60
MW-0.4	6.72	5.2	77
MW-0.7	11.72	10.2	87
MW-1	16.81	10.0	60
MD-0.4	6.72	2.5	37
MD-0.7	11.72	6.0	51
MD-1	16.81	6.3	37

[a] Initial weight of MoO_3 (g/100 g Al_2O_3).
[b] Weight of MoO_3 disappeared (g/100 g Al_2O_3).
[c] Dispersion (ratio between values in Columns 2 and 3).

The Raman spectra of all these systems only show characteristic MoO_3 bands. These results are consistent with data obtained by XRD, because the relative area of the most intense XRD peak for crystalline MoO_3 (recorded at 326 pm) in mechanical mixtures is as much as six times that for samples prepared for impregnation. This increase in residual MoO_3 is large enough to make polymolybdate species undetectable by Raman spectroscopy.

The fact that the dispersion of the supported species is favoured by the presence of water vapour (see Table II) can be explained via the reaction

$$MoO_3 + H_2O \rightarrow MoO_2(HO)_2 \qquad (1)$$

as shown by Glemser and co-workers [25–27], who suggested that the mobile species was the oxyhydroxide $MoO_2(OH)_2$. Leyrer *et al.* [28] assumed that the $MoO_2(OH)_2$ species reacted with surface hydroxyl groups according to

$$MoO_2(OH)_2 + 2OH^- \rightarrow MoO_4^{2-} + 2H_2O \qquad (2)$$

The tetrahedral surface molybdate species thus formed would then polymerize to yield surface polymolybdate species.

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