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Surface Species Formed upon Supporting Molybdena on Alumina by Mechanically Mixing Both Oxides

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MoO_3/Al_2O_3 mechanical mixtures have been prepared with MoO_3 loadings ranging from 0.1 to 2 monolayers (S_{BET} of the support 105 m^2/g), and calcination at 770 K for 8 and 24 h, in the presence and in the absence of water vapour, in order to assess the nature and distribution of the surface species formed. The interaction between the supported phase and the support and the nature of the species formed thereby have been followed through changes in the zero-point-charge (ZPC) of the solids, X-ray diffractograms, and temperature-programmed reduction profiles. The ZPC of the samples changes from 8.8 (parent alumina) to a final value of 3.0 in all samples, but this value is reached at different molybdenum loadings depending on the preparation method. For samples prepared by calcining both oxides in air for 24 h, a monolayer distribution of polymolybdate species is found for molybdenum loadings up to 0.7–0.8 monolayer. With samples calcined for 8 h in air or in dry oxygen, a complete coverage of the alumina surface is achieved only for 2-monolayer loadings.

INTRODUCTION

Catalysts based on molybdena supported on γ-Al_2O_3 are well known in hydrotreating processes. These catalysts are usually prepared by impregnation techniques, as these methods seem to be the most adequate to obtain highly dispersed systems. Among these catalysts, the so-called "monolayer catalysts" deserve special attention. In these catalysts the amount of supported phase is that corresponding to a complete covering of the surface of the support. However, it has been claimed that two types of monolayer catalysts can be defined: those where such a covering corresponds to the "geometrical" covering of the surface and those where the amount of supported phase corresponds to that chemically anchored on the surface of the support. As reaction between the support and the supported phase usually takes place through the hydroxyl groups of the former, the monolayer catalyst would be, in this case, that containing the amount of supported phase that would exactly react with all the reacting hydroxyl groups of the support (*1*, *2*). However, catalysts with similar performance can also be prepared by mechanically mixing both oxides (*3–5*).

Although there have been some studies on the formation of a multilayer or a monolayer on MoO_3/Al_2O_3 samples prepared by different impregnation methods (*6*, *7*), the distribution of molybdena on the alumina surface on samples prepared by mechanical mixtures has not been studied so widely.

With regard to catalysts prepared by mechanical mixtures, Xie *et al.* (*3*) have measured their monolayer capacities on the basis of the residual MoO_3 crystalline phase

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in the samples; calcination of MoO_3/Al_2O_3 physical mixtures (MoO_3 content below the geometrical monolayer capacity) led to vanishing of the molybdena crystalline phase after heating the samples below the melting point of MoO_3. The monolayer capacity value determined by X-ray diffraction (XRD) for these samples is in good agreement with that calculated from a close-packed monolayer model, and evidence for this monolayer model has also been obtained by these authors from X-ray photoelectron spectroscopy.

These same authors (*4*) interpreted the monolayer dispersion of an oxide on the surface of a support on the basis of a transport mechanism by surface diffusion in a concentration gradient. However, Haber *et al.* (*8, 9*) rejected this type of dispersion mechanism and assumed that wetting of one solid by another one must be considered the dominant process for describing the dispersion mechanism, the change in surface free energy being the driving force for the migration of one oxide on the surface of another oxide.

Knözinger and co-workers (*5, 10, 11*) have reported that dispersion of MoO_3 on Al_2O_3 obtained from physical mixtures occurs in the absence and in the presence of water vapour, and they suggest solid–solid wetting as the most likely spreading process. From ion scattering spectroscopy (ISS) data, they found that MoO_3 tends to form "monolayers" on Al_2O_3 surface (*11*), as suggested by Xie *et al.* (*3*).

In this paper, XRD, electrophoretic measurements and temperature-programmed reduction (TPR) have been used to obtain additional information on the spreading process in MoO_3/Al_2O_3 samples prepared by calcination of mechanical mixtures, both in dry O_2 and in air. The MoO_3 distribution on the alumina surface is investigated using electrophoretic migration measurements, a technique which was proved to be very sensitive to variations in surface coverage for a number of supported catalytic systems (*12–14*). Taking into account the different zeta potential (or zero-point-charge, ZPC) values for both series of samples, an explanation for such different behaviour is presented.

EXPERIMENTAL

An Aluminoxid C γ-alumina from Degussa (batch RV005) with a BET specific surface area of 105 $m^2\,g^{-1}$ was used as support. Before incorporation of molybdena, it was calcined overnight at 770 K to eliminate adsorbed organic impurities. MoO_3 was prepared by thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (AHM, from Carlo Erba) at 770 K in air for 5 h.

The physical mixtures were prepared by manually grinding MoO_3 and Al_2O_3 in an agate mortar for 20 min. These samples were calcined at 770 K for different periods of time, 8 and 24 h, following two different procedures in a quartz reactor under a dry O_2 (from Sociedad Castellana del Oxígeno, Spain, 99.95%, passed through a Superpure Gas Purifier model H, from Alltech, to remove impurity traces) flow (30 ml/min), leading to samples MD, and in a static, uncontrolled atmosphere in an open crucible, leading to samples MO. With this, two series of samples have been obtained, in order to investigate the effect of the water vapour pressure on the nature and dispersion of surface molybdate species. In all cases, the relative amounts required for loadings ranged from 0.1 to 2 geometrical monolayers of MoO_3, as calculated from the specific surface area of the support calcined at 770 K (105 $m^2\,g^{-1}$) and the area covered by a "molecule" of MoO_3, 15 × 10^4 pm^2 (*15*). With this, one monolayer equals 16.81 g MoO_3/100 g γ-Al_2O_3.

Chemical analysis for molybdenum was carried out by atomic absorption (AA) in an ELL-240 Mark 2 instrument. X-ray diffraction (XRD) patterns were recorded on a Siemens-500 diffractometer with Ni-filtered Cu $K\alpha_1$ radiation (λ = 154.05 pm) and interfaced to a DACO-MP data acquisition microprocessor provided with Difract/AT software. Zeta potential measurements were carried out in a Zeta-meter Inc. instru-

TABLE I

Chemical Composition, Dispersion Percentage, Isoelectric Point (IEP), Zero-Point-Charge (ZPC), and Apparent Surface Coverage (ASC) of MO and MD Samples

Sample	Initial[a]	Dispersion (%)[b]		IEP	ZPC		ASC	
		8 h	24 h		8 h	24 h	8 h	24 h
Al_2O_3	—	—	—	8.8	—	—		
MoO_3	—	—	—	2.9				
MO-0.1	1.68	—	—		—	7.1		37
MO-0.25	4.20	—	—		—	6.3		52
MO-0.4	6.72	90	95		5.7	3.8	62	90
MO-0.7	11.7	90	95		4.0	3.3	87	96
MO-0.8	13.4	90	95		4.0	3.1	87	99
MO-1	16.8	75	75		3.9	3.0	88	100
MO-1.3	21.8	55	55		3.7	3.0	91	100
MO-1.6	26.9	45	45		3.4	3.0	95	100
MO-2	33.6	35	35		3.0	3.0	100	100
MD-0.4	6.72	45	48		7.4	7.2	31	35
MD-0.7	11.7	62	62		5.4	5.0	66	72
MD-1	16.8	42	42		4.5	4.1	80	86
MD-2	33.6	21	21		3.0	3.0	100	100

[a] Initial weight of MoO_3(g/100 g γ-Al_2O_3).

[b] Dispersion (ratio between g of MoO_3 disappeared and initial g of MoO_3).

ment (Model ZM-77) using 200 mg of 2 μm samples dispersed in 200 ml of 10^{-3} M KCl solutions. The pH was adjusted with either 10^{-2} M KOH or HCl solutions. The zeta potentials were obtained from electrophoretic migration rates using the Smoluchowski equation (*16*). Temperature-programmed reduction (TPR) 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 and a heating rate of 10 K/min. Good resolution of the different reduction steps under these experimental conditions was ensured by using sample weights containing ca. 100 μmol MoO_3 (*17*).

RESULTS AND DISCUSSION

The values obtained from chemical analysis for molybdenum contents in all samples calcined at 770 K for both time periods coincide with the initial ones (see Table 1). In the same table, relevant data for the samples are included.

The percentage of dispersion of MoO_3/Al_2O_3 samples, calcined either in a dry O_2 flow or in a static open atmosphere, has been determined from quantitative XRD measurements of the residual crystalline MoO_3 phase in the samples. A calibration curve has been previously obtained from the area of the residual crystalline MoO_3, measuring the intensity of the relevant peak (recorded at 326 pm) for uncalcined samples, with molybdena contents ranging from 0.1 to 2 monolayers (1.68 to 33.62 g MoO_3/100 g γ-Al_2O_3).

The change in the percentage of dispersion values in MO samples calcined for 8 or 24 h can be explained as follows. For samples MO-0.4, MO-0.7, and MO-0.8 a high dispersion percentage of molybdena is attained (93 ± 3%) and it remains nearly constant with the calcination time. The relatively "low" dispersion percentage for sample MO-1 (75%) does not necessarily indicate a lower dispersion degree than that found for MO-0.7 sample, but it means that the uppermost dispersion capacity of the support has been reached (the alumina surface has been "saturated"). The value for the maximum dispersion attained in our samples is 0.126 g MoO_3/g γ-Al_2O_3 and, taking into account the specific surface area of the support, this amount represents 0.12 g MoO_3/100 m^2 γ-Al_2O_3; that is, formation of ca. 0.72 theoretical geometrical monolayer. The amount of MoO_3 that exceeds this value remains as a crystalline phase, which amount increases from sample MO-0.8 to sample MO-2. Similar values have been reported for the uppermost dispersion capacity by Xie *et al.* (*3*) in MoO_3/Al_2O_3 samples (0.12 g MoO_3/100 m^2 γ-Al_2O_3) prepared by mechanical mixtures, and by Grimblot and co-workers (*18*) for MoO_3/Al_2O_3 catalysts prepared by impregnation (0.115 g MoO_3/100 m^2 γ-Al_2O_3). It should also be noted that the value calculated here for the uppermost dispersion capacity and the ones reported by Xie *et al.* and Grimblot and co-workers are in good agreement with that calculated assuming that MoO_3 forms a close-packed monolayer on the surface of γ-Al_2O_3 (0.12 g MoO_3/100 m^2 Al_2O_3). Hence, we may conclude that monolayer is certainly one of the common forms of the molybdenum-containing species dispersed on the surface of the alumina support.

From the above results we also concluded that the uppermost dispersion capacity (74 ± 3%) does not depend on the method of preparation (impregnation or mechanical mixture), if calcination of mechanical mixtures takes place in the presence of water vapour (*19*).

For samples belonging to series MD, the percentages of dispersion are lower than those found for MO samples. The maximum dispersion is attained for samples MD-0.7, but this value, 0.072 g MoO_3/g γ-Al_2O_3, is much lower than that calculated for samples belonging to series MO, 0.126 g MoO_3/g γ-Al_2O_3. Thus a lower molybdena dispersion degree and a nonmonolayer distribution of MoO_3 on the Al_2O_3 surface is achieved when samples are calcined in the absence of water vapour.

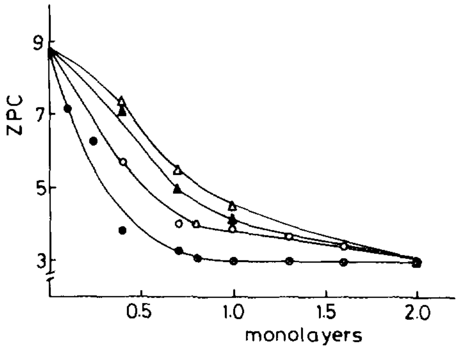

FIG. 1. Zero-point charge curves (ZPC): MO samples (circles) and MD samples (triangles). The calcination time was 8 h (open symbol) or 24 h (filled symbols).

Another conclusion that can be drawn from data in Table 1 is that the percentages of dispersion for both series of samples, MO and MD, when calcined for 8 h are only slightly lower than those obtained upon calcination for 24 h, suggesting that spreading of MoO_3 on the surface of Al_2O_3 seems to be already complete in 8 h (*19*). This calcination time coincides with that reported by Knözinger and co-workers (*10, 11*) for MoO_3/Al_2O_3 catalysts prepared under similar conditions to those used in this work, these authors having used ISS for analyzing the spreading process.

Electrophoretic migration measurements have been used to assess our results on the dispersion process obtained by XRD in the MoO_3/Al_2O_3 samples and also to investigate the way in which molybdena is present on the alumina surface in the calcined samples.

Table 1 shows the experimental values for the zero point charge (ZPC) of samples belonging to series MO and MD and the isoelectric points (IEP) of MoO_3 and γ-Al_2O_3; Fig. 1 shows the zeta potential curves vs molybdena loading in both series of samples. The ZPC values for MO samples calcined 24 h show a sharp decrease from 8.8 (unloaded alumina) to a given value (3) which remains constant for molybdena loadings ranging from 0.8 to 2 monolayers. A steady decrease in the ZPC values is observed in all other samples, dropping to 3 at larger molybdena content (2 monolayers).

The behaviour observed in the ZPC variation in all samples is in agreement with that described by (*12*)

$$\mathrm{ZPC} = (\mathrm{IEP})_S X_S + (\mathrm{IEP})_M X_M, \quad (1)$$

which relates the ZPC of a supported system with the surface molar fractions (X) and isoelectric points (IEP) of the support (S) and the supported species (M), respectively. Assuming that bulk and supported MoO_3 exhibit the same IEP value (3.0), the decrease of the ZPC observed for samples MO and MD from that for unloaded Al_2O_3, $(\mathrm{IEP})_s = 8.8$, should give a measure of an increasing coverage of the surface of alumina by molybdena.

In order to obtain a better comprehension of Fig. 1, it is necessary to analyze the behaviour of each curve separately. While the ZPC value drops to 3 in MO samples calcined for 24 h for a molybdena content of 0.8 monolayer, larger molybdena loadings are needed to achieve such a low ZPC value for the other series of samples. This behaviour implies that a different distribution of molybdena on Al_2O_3 surface takes place as a result of varying the preparation conditions.

At this point we remark that different molybdenum species exist in our samples, as has already been shown by using Laser Raman spectroscopy (*19*). While polymolybdate species are detected in MO samples with molybdena loadings lower than 0.7 monolayer and calcined in the presence of water vapour for 24 h or longer periods of time, such species are not observed when samples are calcined for shorter periods or when they are calcined in the absence of water vapour. In the latter samples, Raman spectra showed the bands of crystalline MoO_3 only.

The conclusion is that the nature and distribution of molybdenum species in these samples is as follows. Polymolybdate species exist on the Al_2O_3 surface for molybdena loadings lower than 0.7 monolayer in MO samples calcined for 24 h. For loadings corresponding to 0.8 monolayer, the alumina surface is completely loaded, and for more than 0.8 monolayer MoO_3 stands on top of the previous layer forming multilayers. In all other samples, "dispersed" molybdena and crystalline MoO_3 exist on the Al_2O_3 surface, progressively covering the support surface as the molybdena loading is increased. The steady decrease in the ZPC values with MoO_3 content from 0.8 to 2 monolayers up to a value of 3 is evidence for the formation of the multilayer.

The final aim of the study is to analyze how the surface of alumina is progressively covered by molybdenum-containing species as loading is increased, and under the different experimental conditions used here. In order to assess this, an alternative approach, from the experimental values so far obtained, can be made through the "apparent surface coverage" (ASC), which is a measure of the percentage of suport surface that is effectively covered by supported species. These values are calculated by

$$\%\mathrm{ASC} = \frac{M_S^{-1}(\mathrm{IEP}_S - \mathrm{ZPC})}{(M_M^{-1} - M_S^{-1})(\mathrm{ZPC} - \mathrm{IEP}_S) + M_M^{-1}(\mathrm{IEP}_S - \mathrm{IEP}_M)} \times 100, \quad (2)$$

where M_M and M_S represent the molecular weights of the supported phase and the support. The values calculated are included in Table 1, and are ploted in Fig. 2 vs the molybdena loading (in monolayers).

As Fig. 2 clearly shows, 100% surface coverage is attained for sample MO-0.8 calcined for 24 h; such a situation is not ob- for the other series of samples, where the maximum surface coverage is only attained when the molybdena content equals 2 monolayers.

The nature of the species existing in these systems prepared by mechanical mixture is

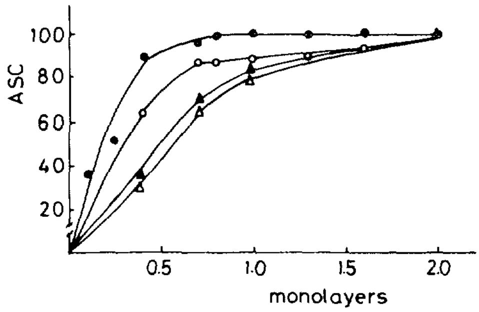

FIG. 2. Apparent surface coverage (ASC): MO samples (circles) and MD samples (triangles). The calcination time was 8 h (open symbols) or 24 h (filled symbols).

the same, up to a given molybdenum loading, as that of the samples prepared by impregnation (*20*); one can conclude that also the distribution of these species on the surface of alumina is similar in both series of samples. However, previous results of López Cordero *et al.* (*21*) with samples prepared by impregnation containing 6–18% MoO_3 on a 230 m^2/g γ-Al_2O_3 (in these circumstances one monolayer is equivalent to 0.35 g MoO_3/1 g Al_2O_3) indicate that a new phase builds up on the alumina surface before this is completely covered with dispersed molybdena. These authors have reported a steady decrease of the ZPC as the MoO_3 content is increased up to 10% MoO_3, the ZPC value maintaining a constant value up to 15% MoO_3 (it should be noted that these MoO_3 percentages cannot be linearly related to ours, as two different samples of alumina with very different specific surface area values are used in both cases), thus concluding that in this loading range (10–15%) MoO_3 particles form multilayers on the alumina surface.

The nature and dispersion degree of the species formed upon supporting molybdena on alumina differ according to the preparation method, although it has been claimed (*11*) that systems prepared by mechanically mixing the oxides, but in the presence of water vapour, are similar to those prepared by impregnation. In any case, it should be expected that such differences should also turn up on studying the reducibility of these samples. The study of such a reducibility is of paramount importance, as these systems, when acting as catalysts in selective oxidation processes, usually undergo oxidation/reduction reactions. In our case, reducibility of the samples has been assessed by TPR. The profiles for MO and MD samples are given in Fig. 3 and the results have been summarized in Table 2. From the hydrogen consumptions and molybdenum loadings, the average H_2/Mo results to be 2.7 ± 0.3 and so it can be assumed that the final oxidation state of the molybdenum species is Mo^0. The inset in Fig. 3 corresponds to the reduction profile of bulk MoO_3. Reduction starts at 825 K. The sharp features in this profile are due to the simultaneous melting of MoO_3 (m.p. = 1068 K), and thus the kinetics of reduction of the liquid differ from that for the solid.

However, the reduction profiles for both series of samples are rather different. For MO samples, a first reduction peak is recorded for MO-0.4 at 725 K, which shifts to 750 K for MO-0.7 and MO-1. In addition, a reduction process should take place from ca. 850 K upwards. The profiles for MO-0.4 and MO-0.7 in the high-temperature range are rather similar, but ill-defined shoulders start to develop above ca. 850 K, and the intensity of the peak at ca. 750 K increases for MO-0.7. It should be noted that the intensity of this peak remains constant for MO-0.7 and MO-1, and in the latter sample a new peak develops at 925 K, together with a complex feature at higher temperature, which coincides with that recorded for bulk MoO_3.

Taking into account our previous Raman spectroscopy results (*19*, *22*), it can be concluded that the peak at ca. 725–750 K and the peaks at higher temperatures recorded for this sample are due to reduction of dispersed polymolybdate species. It should be stressed that Raman spectroscopy is specially sensitive to the presence of bulk MoO_3, and that a small amount of this would avoid detection of peaks due to dispersed

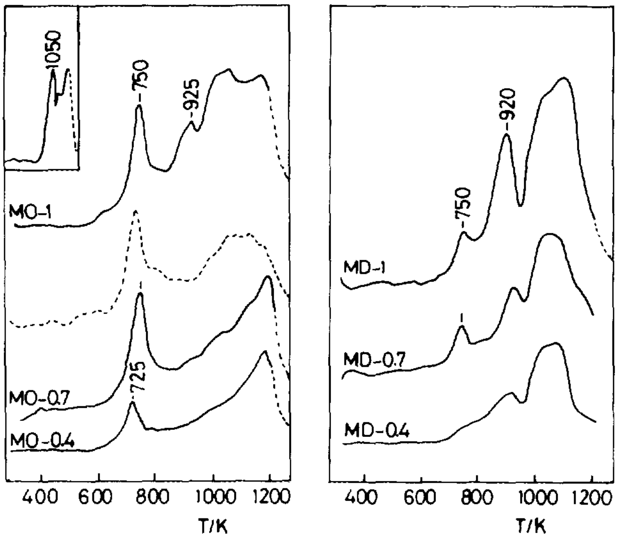

FIG. 3. TPR profiles of MO and MD samples calcined for 24 h (dotted line for sample MO-0.7 calcined for 48 h). Insert: bulk MoO_3.

species. Thus, as the Raman spectrum for this sample shows only bands due to dispersed polymolybdate species, we can conclude that no other molybdenum-containing species exists in sample MO-0.4. With this, detection of two reduction maxima cannot be ascribed to reduction of two different species; on the contrary, from the integrated areas of peaks at 725 and 1000 K for this sample, whose ratio is close to 0.5, it can be tentatively assumed that they correspond to the two-step reduction process $Mo^{6+} \rightarrow Mo^{4+} \rightarrow Mo^0$. A similar two-step reduction process has been reported by Caceres *et al.* (*23*) for MoO_3/Al_2O_3 catalysts prepared by equilibrium adsorption. These authors have shown that for low solute concentration the molybdenum-containing species become highly dispersed on the support surface, mostly as tetrahedrally coordinated species, while at high solute concentrations the surface of the carrier becomes covered with both tetrahedrally and octahedrally coordinated species, present as monolayers or multilayers, respectively.

TABLE 2

Summary of TPR Data

Sample	H_2/Mo[a]	Total H_2 consumption (μmol/g)
MO-0.4	3.0	1429
MO-0.7	2.6	2141
MO-1	2.6	3099
MD-0.4	2.7	1241
MD-0.7	2.5	1992
MD-1	2.6	2987

[a] Atomic ratio.

Development of ill-defined shoulders at 850 K for sample MO-0.7 is due to reduction of MoO_3, in agreement with the Raman spectroscopy results (*20*). When this sample is calcined for 48 h (where Raman spectra show exclusively the presence of polymolybdate species), the peak at 750 K and the shoulder at 850 K remain, but the peak at very high temperature vanishes. The integrated area of the peak at 750 K for reduction in sample MO-0.7 when calcined for 24 or 48 h is constant (570 ± 10 μmol H_2/g solid). In addition, these results confirm our previous assumption concerning the presence of both MoO_3 and polymolybdate species in sample MO-0.7 in spite of the fact that the presence of a very small percentage of the former does not permit detection of the latter by Raman spectroscopy. For these samples (MO-0.7 and MO-1.0) the ratio of the integrated areas of the peak at 750 and 1100 K is larger than 0.5, as the presence of MoO_3 (which reduces above the maximum temperature that can be experimentally reached) leaves part of molybdenum species unreduced. In fact, the hydrogen consumptions for these two samples are 2.6, while for sample MO-0.4 it was 3.0.

For MD samples, XRD results indicate the presence of dispersed MoO_3, as concluded from the intensities of its main diffraction peaks. Hence the reduction peak at ca. 920 K should be due to dispersed MoO_3, while reduction of bulk MoO_3 would account for the very-high-temperature reduction peak at ca. 1100 K. However, the presence of the peak at 750 K, due to polymolybdate species, is somewhat unexpected. According to data in the literature (*11*) polymolybdate species are formed through hydration of MoO_3 to yield $MoO_2(OH)_2$ and further anchoring of these species through reaction with surface hydroxyl groups, dehydration and subsequently polymerization. As these samples have been prepared under "dry" conditions, these species should not have been found. However, it should be noted that, on preparing this series of samples, O_2 flow was passed through the samples with simultaneous temperature increasing, and so a small amount of adsorbed water should remain on the Al_2O_3 surface (*11*). Under these experimental conditions, partial reaction of MoO_3 with H_2O cannot be discarded, thus leading to formation of a small amount of dispersed polymolybdate species in samples MD-0.7 and MD-1.0.

The results reported here for the TPR analysis of the samples prepared by mechanical mixture are rather different from those reported for samples prepared by different impregnation methods (*24*). For samples prepared by adsorption from the liquid phase or by wet or dry impregnation, Thomas *et al.* have reported (*24*) TPR patterns with low-temperature features ascribed to reduction of molybdate layers. For samples prepared by impregnation at different pH's López-Cordero *et al.* (*21*) have proposed a two-step reduction process, ascribing the first peak to the first reduction step ($Mo^{6+} \rightarrow Mo^{4+}$) of octahedrally coordinated molybdenum species, mainly as multilayers, with some polymolybdates in monolayer patches.

CONCLUSIONS

From the XRD data above we conclude that the dispersion process seems to be complete in less than 8 h either in air or in a dry O_2 flow, so the use of a larger calcination time does not increase the percentage of dispersion. Nevertheless, electrophoretic measurements show that the estimation of 8 h to complete the dispersion process is not right, as in such a case both curves for MO samples and both curves for MD samples (see Fig. 1) should be coincident, respectively. However, the data fall into four well differentiated curves, one for each series of sample preparation. This means that a calcination time of 8 h is not enough to achieve a constant percentage of dispersion on the support surface, either in the presence or in the absence of water vapour.

Different molybdenum species and a different distribution of such species on the alumina surface (monolayer or multilayer) are detected by Laser Raman, ZPC, XRD, and TPR measurements.

The value of 0.12 g $MoO_3/100\ m^2\ \gamma\text{-}Al_2O_3$ (0.72 theoretical monolayer) for the uppermost dispersion capacity in samples MO calcined for 24 h, obtained by XRD, coincides within experimental error with that found by ZPC measurements (0.8 monolayer).

With this, the scheme illustrated in Fig. 4 would account for the situation in these samples, according to the calcination time, the molybdena loading and the experimental conditions. For MO samples, on increasing the calcination time MoO_3 transforms to

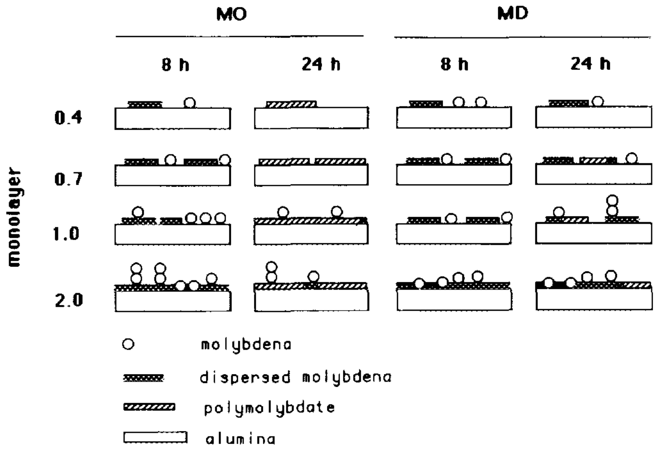

FIG. 4. Scheme showing the dispersion of molybdenum-containing species on the surface of alumina.

polymolybdate species, increasing the surface coverage. When these samples are calcined for 24 h, the surface of the support is completely covered when the molybdena loading is equivalent to 0.7–0.8 monolayers; the remaining molybdena exceeding this quantity remains on the polymolybdate monolayer, both in the crystalline and dispersed state, leading to multilayer formation. If calcination is carried out only during 8 h such a transformation to polymolybdates does not take place, but the alumina surface is progressively covered by crystalline and dispersed alumina on increasing the molybdena loading, covering being complete for a loading equivalent to 2 monolayers.

For MD samples, calcination for 8 h leads to a similar situation to that found for MO samples calcined for the same time. However, on calcining for 24 h, in addition to crystalline and dispersed molybdena, a small amount of polymolybdate species also exist, according to our TPR results. Formation of this species takes place because of the presence of small amounts of water vapour, as the samples were not degassed by flowing argon or any other inert gas, before increasing the temperature and calcination.

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