

Effect of the preparation method on the reducibility of molybdena–alumina catalysts

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Abstract

Two series of molybdena–alumina catalysts were prepared. The first series was prepared by the incipient wetness procedure (1.7–8.8 wt.% Mo) (series IW). A second series was obtained using the equilibrium adsorption (1.3–8.2 wt.% Mo) (series EA) method. X-ray photoelectron spectroscopy (XPS) was used to study the distribution of Mo oxidation states. The average Mo oxidation state estimated from XPS agreed with that obtained by measuring the O₂ consumption on reoxidation, for a given catalyst. The chemisorption of oxygen at –78°C and the isomerization of 1-butene were performed as probes for assaying the number of coordinatively unsaturated sites created by the reduction process. These studies were conducted in order to study possible changes in Mo speciation or distribution, relevant to catalytic reactions, which may occur as a result of the specific features of the preparation method (EA vs. IW). The results showed that for both series of solids, the reducibility of the molybdenum species increases as the metal loading increases, in agreement with the literature. For catalysts with similar loading, the IW series showed a higher degree of reduction with a concomitant increase in the relative abundance of Mo(IV) species attributed to paired double-bonded Mo(IV) entities (as in MoO₂). The reducibility data were consistent with the catalytic results and the oxygen chemisorption results. IW preparations (with similar Mo loading) were more active towards the isomerization of 1-butene and chemisorbed larger amounts of oxygen than their EA counterparts. The differences in reducibility can be ascribed to a nonuniform repartition of the molybdenum species between the external and internal surfaces of the alumina, for the IW preparations. Another possible explanation may stem from a decoration effect of the molybdenum species by Al(III) ions. The latter may arise from dissolution of the alumina, which is favored on the EA series due to the long contact time between the solution of the Mo promoter and the support. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: X-ray photoelectron spectroscopy; XPS; Mo oxidation states; Molybdena reducibility

1. Introduction

Molybdena–alumina catalysts have been the subject of numerous studies due to their role in different important catalytic reactions, which include hydrotreating and hydrodesulfurization

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[1–3]. Different methods have been described in the literature for the preparation of these catalysts [4–20]. Among these, the incipient wetness (IW) and the equilibrium adsorption (EA) methods have been widely used [7–37]. The former involves contacting the support with a solution containing the precursor salt using a predetermined volume of water sufficient to fill the pores. Due to the short contact time between the support and the molybdenum solution, inhomogeneities in the repartition of the Mo phase may occur. The EA method consists of adsorbing Mo from dilute aqueous solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ at a fixed pH over an extended period of time (~ 3 –4 days). The loading is controlled by varying the pH of the Mo solution. In principle, a more homogeneous repartition of the Mo phase should be obtained for the EA series.

As expected from their industrial importance, molybdena–alumina catalysts have been characterized by an array of different experimental techniques [1,7,21–38]. In particular Laser Raman spectroscopy (LRS) has proven very useful for the determination of the molecular structure of the different species present on the oxidic catalysts. Recent LRS studies by Wachs [15], indicate that the preparation method does not influence the molecular structure of the oxidic molybdenum species present over the alumina. Thus, for a given Mo loading, the nature of the Mo species is essentially independent of the preparation method. It is not clear, however, how the specifics of a given preparation method may induce subtle changes in the Mo speciation. These differences may be difficult to detect by a spectroscopic method but, nonetheless, be catalytically important. One approach to assay these changes is to compare the reducibilities of Mo samples obtained by different methods (ex: IW vs. EA). Previous studies of the reducibility of Molybdena–alumina catalysts have been conducted mainly by isothermal reduction–oxidation (redox) cycles [2,34,38–41], temperature programmed reduction (TPR) [7,18,42–46] and X-ray photoelectron spec-

troscopy (XPS) [24,25,38,47–49] on different EA and IW preparations. However, a *comparative* study of the reducibility of molybdena–alumina catalysts prepared by the EA and IW methods is lacking. The lack of these studies was the driving force for the present paper.

The main purpose of the work was to investigate possible changes in Mo speciation or distribution, relevant to catalytic reactions, which may occur as result of the specific features of the preparation method. Such differences were assayed by comparing the reducibility of two series of molybdena–alumina catalysts prepared by EA and IW methods. The extent of reduction of the molybdenum phase was estimated from XPS results and redox measurements. The isomerization of 1-butene and the chemisorption of O_2 at -78°C were performed as probes for assaying coordinatively unsaturated sites created by the reduction process.

2. Experimental

γ -Alumina (Ketjen CK-300), surface area $210 \text{ m}^2/\text{g}$, was used as the support. The IW catalysts (1.7–8.8 wt.% Mo) were prepared by impregnating with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (BDH, reagent grade) to incipient wetness. The EA solids were prepared by the adsorption equilibrium method devised by Wang and Hall [7,8]. The preparation procedure was identical to that used in Ref. [8]. The different Mo loadings (1.3–8.2 wt.% Mo) were obtained by varying the initial pH of the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ solution. Table 1 summarizes the preparation data. These results have been partially reported

Table 1
Chemical composition and preparation parameters for the molybdena–alumina catalysts prepared by the equilibrium adsorption method

Catalyst	Initial pH	Final pH
1.3% Mo(EA)	8.7	8.3
3.9% Mo(EA)	5.5	6.4
6.0% Mo(EA)	4.0	5.7
8.2% Mo(EA)	2.0	3.6

elsewhere [35]. All the solids were dried for 2 h at 100°C and calcined for 5 h at 500°C. The Mo loading was determined by atomic absorption spectroscopy.

The experimental procedure for the XPS experiments has been reported previously [38]. It will be repeated for the sake of completion. XPS spectra of the reduced catalysts were obtained with a modified AEI ES200 spectrometer equipped with an aluminum anode (Al $K\alpha = 1486.6$ eV) at a power of 240 W (12 kV and 20 mA). The catalysts were pressed as pellets at 2000 kg/cm² and mounted on a sealable probe which permitted transfer of the reduced catalyst from an external reaction chamber to the spectrometer without exposure to air. The catalysts were reduced under flowing H₂ (40 cc/min) at 500°C for 2 h. The spectrometer was interfaced to an IBM PC compatible for data collection. The subsequent data analysis was also carried out in the PC environment under DOS, using programs (GOOGLY software) written in house [50]. A damped nonlinear least-squares fitting (NLLSF) routine was used to curve fit the Mo 3d envelopes. The binding energy (BE) values were referenced to the Al 2p line (74.5 eV). The methodology used for curve fitting the Mo 3d envelope and the assumptions made for quantitative analysis of Mo oxidation states, in molybdena–alumina catalysts, is similar to that used previously [25,38,51]. The BE and fwhm values for the Mo(VI) 3d doublet were obtained from the XPS spectra of the oxidic catalyst. The XPS parameters found for the Mo(V) and Mo(IV) were a result of the curve fit procedure. As mentioned previously [38], it should be noted that two binding energy values have been reported for Mo(IV) [52–55]: A high binding energy value (Mo 3d_{5/2} 231.5–232 eV) attributed to ionic ‘isolated’ Mo(IV) and a low binding energy value (Mo 3d_{5/2} ca. 230 eV) typically associated with Mo(IV) as in MoO₂ and ascribed to paired double-bonded Mo(IV). Since the high binding energy value is comparable to that typically used for Mo(V), one cannot rule out that the Mo 3d doublet attributed to

Mo(V) is in fact a convolution of the contributions from Mo(V) and ionic Mo(IV). Thus, in this work, for the sake of simplicity, Mo(V) (Mo 3d_{5/2} BE: 231.5–231.6 eV) will refer to Mo(V) and ionic Mo(IV) whereas Mo(IV) (Mo 3d_{5/2} BE: 229.7 eV) will designate paired double-bonded Mo(IV). This assumption was made on a recent report [38].

The reduction–oxidation (redox) cycles, O₂ chemisorption at –78°C and the catalytic experiments, were performed in an all-glass recirculation system attached to a BET conventional system identical to that used in Refs. [34,35].

The redox cycles were performed in the following way: catalyst samples of approximately 0.5 g were placed in a quartz microreactor and oxidized with pure oxygen (60 cm³/min) at 500°C. The sample was evacuated ($P < 2.10^{-5}$ Torr) for 1 h at 500°C and cooled to room temperature under vacuum. The catalyst was then exposed to pure hydrogen and the temperature increased (5°C/min) up to 500°C. The hydrogen consumption was measured after 2 h (at 500°C) from the pressure drop due to the reduction process. Care was taken to trap the evolved water (reduction subproduct) at –196°C. The reduced sample was then evacuated for 1 h at 500°C and cooled to room temperature under vacuum. The described experimental sequence was repeated with pure oxygen, yielding the oxygen consumption. Due to the reported presence of H_R (reversible adsorbed hydrogen at 500°C) [7], the e/Mo (electrons gained per Mo atom) were determined by measuring the O₂ consumption (at 500°C) required for complete reoxidation to Mo(VI), after the reduction procedure. The average Mo oxidation state (AOS) can be calculated as (6-e/Mo).

The oxygen chemisorption experiments were carried out at –78°C. The catalysts were subjected to a reduction procedure identical to that used in the redox cycles. The double isotherm method of Weller et al. [56–59] was used to calculate the irreversible uptake of oxygen at –78°C over the reduced molybdena–alumina catalysts.

The catalytic experiments were carried out at 58°C. The initial amount of 1-butene used was 50 cc (NTP). The reaction products were analyzed by on-line gas chromatography. The analytical procedures are fully described elsewhere [35]. The initial slopes of the plots of conversion (percentage of each hydrocarbon) vs. time provided the way of calculating initial rates of appearance of the different reaction products. Prior to the reaction, the catalyst was treated with pure O₂ (60 cm³/min) at 500°C for 8 h to condition it. The catalysts were reduced with pure H₂ at 500°C for 2 h and then evacuated at 18°C for 1 h.

3. Results

Fig. 1 shows typical Mo 3d curve-fitted spectra for the reduced 5.5% Mo (IW) and reduced 6.0% Mo (EA) catalysts. As shown, only three sets of Mo 3d doublets were necessary to satisfactorily curve fit the data. The doublets are identified by their oxidation state assignment (Fig. 1). It can be readily seen that there is a shift in the Mo oxidation state distribution towards Mo(IV) in the 5.5% Mo (IW) preparation, compared to that observed in the 6.0% Mo (EA) catalyst. This indicates a greater reducibility of the IW preparation. Similar observations can be made from the comparison of curve-fitted results for the other catalytic systems. For catalysts of a given series, the results indicate, as expected [7,19,24], an increased reducibility of the Mo phase with increasing loading.

Table 2 shows the XPS parameters, BE's and full width at half maximum (fwhm's), obtained for both series of reduced molybdena-catalysts. Similar BE values for the different Mo oxidation states were observed as the Mo loading was varied, irrespective of the preparation method. The fwhm's for the different Mo oxidation states, followed the same pattern as the BE's.

For a more quantitative treatment of the results, the abundance of various Mo oxidation states was measured. The relative abundance of

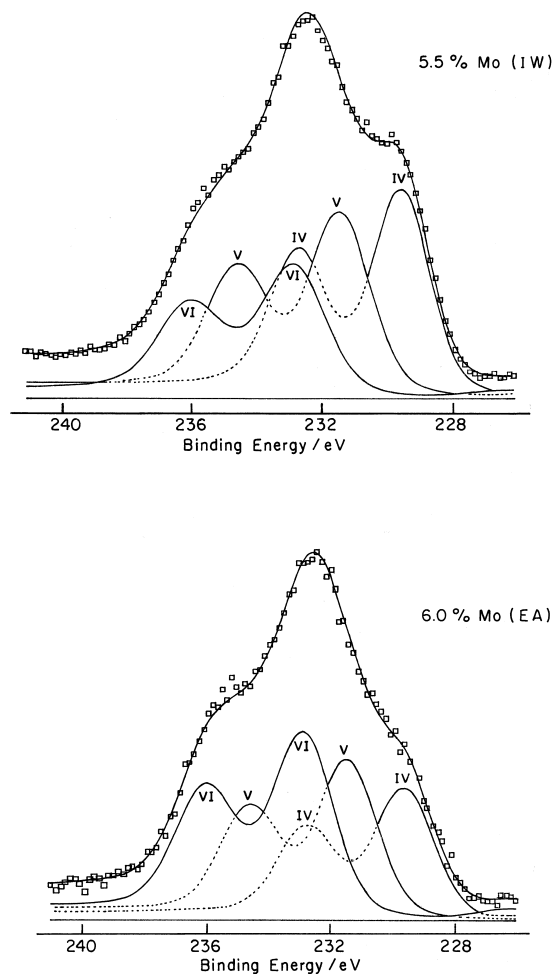


Fig. 1. Mo 3d curve-fitted spectra for reduced 5.5% Mo (IW) and 6.0% Mo (EA) catalysts. The Mo 3d_{5/2}–3d_{3/2} doublets are designated by their assigned oxidation states. For more details see text.

each Mo oxidation state was calculated by dividing the Mo 3d area for a given oxidation state by the total area of the Mo 3d envelope. The results expressed as percentages, are shown in Table 3. It can be seen that for both series of catalysts, the increased reducibility of the Mo phase with increasing loading is reflected in the observed decrease in the percentage of Mo(VI) with increasing Mo loading and the concomitant increase in the relative abundance of Mo(V) or Mo(IV) for both series of solids. For catalysts with similar Mo loading, the higher reducibility of the IW preparations compared with the cata-

Table 2
XPS parameters derived for both series of reduced molybdena–alumina catalysts

Catalysts	Binding energies, eV ^a			fwhm, eV ^c		
	Mo(VI)	Mo(V)	Mo(IV)	Mo(VI)	Mo(V)	Mo(IV)
	3d _{5/2}	3d _{5/2} ^b	3d _{5/2}	3d _{5/2}	3d _{5/2}	3d _{5/2}
1.3% Mo(EA)	233.0	231.3	229.5	2.5	2.4	2.2
3.9% Mo(EA)	232.8	231.4	229.5	2.5	2.3	2.2
6.0% Mo(EA)	232.8	231.4	229.6	2.3	2.3	2.1
8.2% Mo(EA)	232.7	231.4	229.6	2.3	2.2	2.2
1.7% Mo(IW)	232.9	231.6	229.7	2.5	2.3	2.3
3.8% Mo(IW)	232.9	231.5	229.6	2.4	2.2	2.2
5.5% Mo(IW)	232.9	231.5	229.7	2.3	2.2	2.1
8.8% Mo(IW)	232.8	231.6	229.7	2.3	2.1	2.2

^aThe difference between the binding energy values of Mo 3d_{5/2} and Mo 3d_{3/2} was kept constant (3.1 eV) for all oxidation states.

^bMo(V) (Mo 3d_{5/2} BE: 231.5 ± 0.1 eV) refers to Mo(V) and ionic ‘isolated’ Mo(IV) whereas Mo(IV) (Mo 3d_{5/2} BE: 229.7 ± 0.1 eV) designates paired double-bonded Mo (IV). For more details see text.

^cIdentical Mo 3d_{3/2} and Mo 3d_{5/2} fwhm values were used.

lysts prepared by the EA method is illustrated by a lower percentage of Mo(VI) and an increase in the percentage of Mo(IV) species.

From the distribution of Mo oxidation states determined by XPS, the average oxidation state of the Mo phase can be calculated and used as an estimate of the overall reducibility of the catalyst. The results were compared to the values obtained from reoxidation experiments. (Table 4 and Fig. 2). Clearly, a reasonable agreement is found between the values obtained from redox cycles and those estimated from the XPS data. Both methods showed a decrease in the average oxidation state of the Mo phase (e.g., increase in the reducibility) with increasing Mo content. This can be attributed to the increased

relative abundance of easier to reduce polymeric Mo at the detriment of difficult to reduce monomeric Mo species, with increasing Mo loading [7,15,60]. XPS data and redox results also showed that for a given Mo loading, solids prepared by incipient wetness are easier to reduce than those prepared by the equilibrium adsorption method.

Additional evidence for the higher reducibility of IW preparations can be inferred from oxygen adsorption data. Oxygen chemisorption has been widely used for estimation of the coordinatively unsaturated sites (CUS) present on molybdenum based catalysts [41,56–59]. These CUS are usually created by different pretreatment procedures, e.g., reduction, sulfida-

Table 3
XPS abundance of different oxidation states for the two series of Mo/Al₂O₃ catalysts

Catalysts	Mo 3d peak areas, a.u.			Percentage of each oxidation state		
	Mo(VI)	Mo(V)	Mo(IV)	Mo(VI)	Mo(V)	Mo(IV)
1.3% Mo(EA)	424	137	66	67.6	21.9	10.5
3.9% Mo(EA)	925	466	326	53.9	27.1	19.0
6.0% Mo(EA)	1268	1043	850	40.1	33.0	26.9
8.2% Mo(EA)	1460	1347	1350	32.5	32.4	32.5
1.7% Mo(IW)	846	376	170	60.8	27.0	12.2
3.8% Mo(IW)	656	595	452	38.5	34.9	26.5
5.5% Mo(IW)	2835	3699	3917	27.1	35.4	37.5
8.8% Mo(IW)	1636	2080	2580	26.0	33.0	41.0

Table 4
e/Mo in Mo/Al₂O₃ catalysts estimated from O₂ consumption^a and XPS experiments^b

Catalyst	(e/Mo) _{O₂}	(e/Mo) _{XPS}
1.3% Mo(EA)	0.5	0.4
3.9% Mo(EA)	0.6	0.6
6.0% Mo(EA)	0.8	0.8
8.2% Mo(EA)	1.2	1.0
1.7% Mo(IW)	0.6	0.5
3.8% Mo(IW)	1.0	0.9
5.5% Mo(IW)	1.2	1.1
8.8% Mo(IW)	1.6	1.2

^aThe e/Mo for each catalyst was determined by measuring the O₂ consumption (at 500°C) required for complete reoxidation, after the reduction procedure. For more details see text.

^bThe e/Mo for each catalyst was determined from the relative abundance of the different Mo oxidation states. For more details see text.

tion. The results for the oxygen chemisorption experiments are shown in Table 5. It can be seen that for catalysts with similar loading, higher O/Mo ratios are obtained for the IW preparations as compared to their EA-prepared counterparts. These results are in line with the reducibility data and suggest that CUS are easier to form, during the reduction process, on IW solids than on EA catalysts with similar Mo

Table 5
Oxygen chemisorption on reduced molybdena–alumina catalysts^a

Catalyst	O atoms g ⁻¹ × 10 ⁻²⁰	O atoms/ Mo atoms
1.3% Mo(EA) ^b	nd	nd
6.0% Mo(EA)	0.15	0.031
8.2% Mo(EA)	0.59	0.11
1.7% Mo(IW) ^b	nd	nd
5.5% Mo(IW)	0.38	0.11
8.8% Mo(IW)	0.88	0.16

^aExperiments performed at -78°C. For more details see text.

^bNot detected.

loading. Furthermore, in line with the reducibility pattern shown earlier, for both series of catalysts, the O/Mo atomic ratio increases as the molybdenum loading increases.

Isomerization and metathesis of 1-butene were carried out over the reduced molybdena–alumina catalysts. The rationale for performing the catalytic experiments is that previous reports [61,62,60] have shown that the isomerization process proceeds through a hydride insertion mechanism on CUS created by the reduction of an 8% IW molybdena–alumina catalyst. Thus, in principle, the isomerization results can pro-

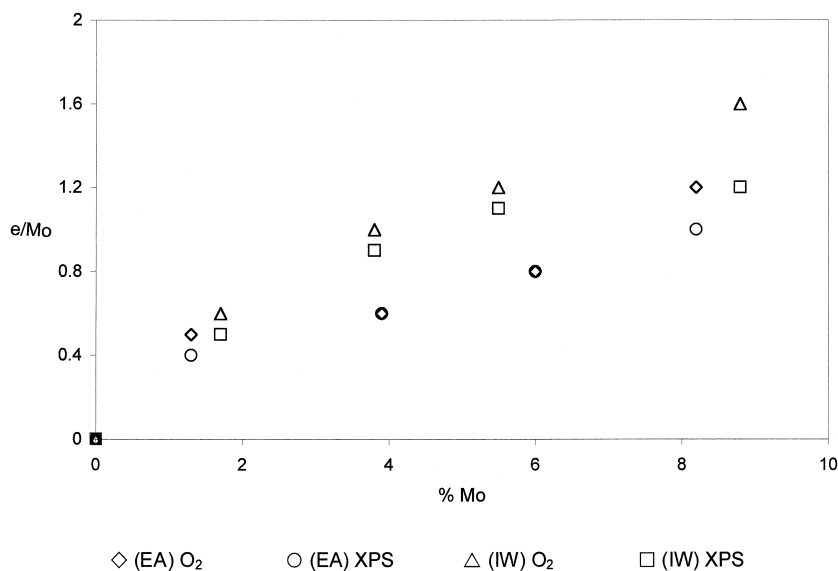


Fig. 2. Plot of e/Mo vs. molybdenum loading for the preparations used throughout this work.

Table 6

Initial rates of formation for the products arising from the isomerization and metathesis reactions over the two series of reduced Mo/Al₂O₃ catalysts^a

Catalyst	C ₂ H ₄	C ₃ H ₆	<i>trans</i> -C ₄ H ₈	<i>cis</i> -C ₄ H ₈	<i>cis</i> + <i>trans</i>	<i>cis</i> + <i>trans</i> ^c
1.3% Mo(EA) ^b	–	–	3.3	5.8	9.1	–
3.9% Mo(EA)	–	–	0.0057	0.0040	0.0097	–
6.0% Mo(EA)	–	0.013	0.093	0.053	0.15	4.8
8.2% Mo(EA)	–	0.016	0.35	0.15	0.50	4.6
1.7% Mo(IW) ^b	–	–	3.6	6.2	9.8	–
3.8% Mo(IW)	–	–	0.011	0.018	0.034	–
5.5% Mo(IW)	–	0.023	0.37	0.17	0.54	4.9
8.8% Mo(IW)	–	0.029	0.56	0.25	0.81	5.1

^a Values expressed in mol/at_{Mo} min.

^b The values for the initial rates of formation of the different products over the 1.3% Mo(EA) and 1.7% Mo(IW) catalysts are expressed in (molec./g_{cat} min) × 10¹⁸. They were similar to those reported for the pure support [35].

^c Values reported in mol/oxygen atom min.

vide a crosscheck on the formation of CUS on the two series of reduced catalysts. The catalytic results are summarized in Table 6. As observed, the formation of the isomerization products (*cis*- and *trans*-2-butene) is strongly favored over the formation of the metathesis products (ethylene and propylene). This result can be accounted for in terms of the presence of H_R, which is known to severely hinder the metathesis transformations while favoring the isomerization process [62] on reduced molybdena–alumina catalysts. It can also be observed that for both series of catalysts, the initial rate of formation of the 2-butenes increases as the Mo loading increases. Moreover, for catalysts with similar Mo loading, the IW preparations were clearly more active than their EA counterparts, for the isomerization reaction. However, when the initial rates are normalized per oxygen atom chemisorbed (see last column of Table 6), the results are almost identical for all the catalysts irrespective of the preparation method.

4. Discussion

The results of the XPS and redox cycles experiments clearly show that the IW preparations are easier to reduce than solids with similar loading, prepared by the equilibrium adsorp-

tion method. The oxygen chemisorption and catalytic results are in line with the reducibility results observed in this work.

This finding may seem, a priori, unexpected, in view of recent reports [15], indicating that the preparation method does not influence the molecular structure of the oxidic molybdenum species present over the alumina. Therefore, a similar degree of reducibility should be expected for both series of solids.

One obvious explanation lies in the possibility of forming minor amounts of MoO₃ in the IW preparations, at loadings below the monolayer value [27,63]. This can be attributed to the inherent imperfection of the IW preparation method. MoO₃ is known to be easier to reduce than surface molybdena–alumina interaction species [41]. Laser Raman spectroscopy (LRS) was shown to be very useful in determining the molecular structure of supported metal oxide species [15]. In addition, the technique is very effective in detecting minor amounts of bulk oxides such as MoO₃ and WO₃, because of their large scattering cross-section. Preliminary LRS work [64] on the catalysts used in the present work has shown no bands characteristic of MoO₃ (815, 663, 335 and 281 cm⁻¹). These results agree with those of Wachs [15], where the appearance of bulk MoO₃ LRS bands occurred at loadings higher than 20 wt.% MoO₃, for a molybdena–alumina series prepared by the

incipient wetness method. The specific surface area of their alumina ($180 \text{ m}^2/\text{g}$), was similar to that used in this work. The aforementioned LRS results allow us to conclude that the higher reducibility displayed by the IW preparations is not due to the formation of MoO_3 .

A somewhat related explanation for the difference in reducibility of the two series of preparations may be based on the reported [36] variation in the repartition of the Mo phase between the external and internal parts of the catalyst particle as a function of the preparation method. Previous ion scattering spectroscopy (ISS) study [36] carried out over the same catalysts used in the present work, showed that the surface coverage of the Mo phase was higher for the IW prepared catalysts than for the corresponding EA preparations. This was attributed to an enrichment of Mo species on the external parts of the alumina surface as a result of a nonuniform repartition of the molybdenum phase in IW preparations. These results can be used to explain the differences in reducibility observed for both series in the present work. Mo-rich outer layers in IW preparations may contain a greater fraction of easy to reduce polymeric species than their more uniform EA counterparts.

An alternative explanation is based on the work of Clause and coworkers [20,65,66]. These authors have studied the deposition of Co(II) and Ni(II) on alumina by different preparation methods. They showed that alumina could be reactive, even at the isoelectric point, forming Al(III) ions. By using a dialysis membrane device and long contact times between a solution of the metal promoter and the alumina, the authors evidenced a dissolution–precipitation phenomena in the vicinity of the alumina surface. Based on these findings, the differences in reducibility can be ascribed to a possible decoration effect of the molybdenum species by Al(III) ions. The latter would arise from the dissolution of the alumina, which is favored on the EA series due to the long contact time between the solution of the Mo promoter and

the support. Recent work [9,11] support these ideas by showing the formation of an Anderson-type alumino heteropolymolybdate during the preparation of molybdena–alumina catalysts.

It must be noted, however, that the observed differences in the reducibility of Mo–alumina catalysts prepared by IW and EA methods, although consistent and catalytically relevant, remain relatively limited. Thus, these findings should not be considered as in conflict with previous studies [15] highlighting, for a given loading, the similarity of Mo species prepared by different methods. The results of the present study should, rather, be considered as an evaluation of the degree of alterations in Mo species, relevant to catalytic reactions, which may arise from the characteristics of a given preparation method.

5. Conclusions

Two series of molybdena–alumina catalysts were prepared. The first series was prepared by the incipient wetness procedure (1.7–8.8 wt.% Mo) (series IW). A second series was obtained using the equilibrium adsorption (1.3–8.2 wt.% Mo) (series EA) method. The distribution of Mo oxidation states was determined on the reduced catalysts by X-ray photoelectron spectroscopy (XPS). The average Mo oxidation state estimated from XPS agreed with that obtained by measuring the O_2 consumption on reoxidation, for a given catalyst. The chemisorption of oxygen at -78°C and the isomerization of 1-butene were performed as probes for assaying the number of coordinatively unsaturated sites created by the reduction process.

The results showed that for both series of solids, the reducibility of the molybdenum species increases as the metal loading increases, in agreement with the literature. For catalysts with similar loading, the IW series showed a higher degree of reduction. The reducibility data

were consistent with the catalytic results and the oxygen chemisorption results. IW preparations (with similar Mo loading) were more active towards the isomerization of 1-butene and chemisorbed larger amount of oxygen than their EA counterparts.

The differences in reducibility can be ascribed to a nonuniform repartition of the molybdenum species between the external and internal surfaces of the alumina, for the IW preparations. Another possible explanation may stem from a decoration effect of the molybdenum species by Al(III) ions. The latter may arise from dissolution of the alumina, which is favored on the EA series due to the long contact time between the solution of the Mo promoter and the support.

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