Spectroscopic Investigation of the Molybdenum Active Sites on Mo^{vi} Heterogeneous Catalysts for Alkene Epoxidation

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Spectroscopic and spectromagnetic investigations on molybdenum centres in $MoO_3 \cdot H_2O$ and its polymersupported form have been carried out. Both were tested as catalysts for cyclohexene epoxidation in a heterogeneous phase; both needed activating pretreatment before the reaction. XPS and EPR data show that the metal is mainly present as MO^{VI} . The activation process increases the acidic character of MO^{VI} and its efficiency depends both on the oxidizing power of the activating reactant and on the accessibility of the metal to the reactant. The steric hindrance of MO^{VI} lowers the catalytic activity owing to the replacement of H_2O by carboxylic groups of the functionalized resin.

The liquid-phase epoxidation of alkenes using homogeneous Mo^{VI} catalysts and alkyl hydroperoxides has become the most important industrial process for the production of hydrocarbon oxides (*e.g.* the Halcon process).¹

In order to recover catalysts easily, many attempts have been made to use molybdenum compounds in the heterogeneous phase,² and also to heterogenize them on functionalized polymeric supports.^{3–8} However, the reaction times required to obtain significant yields of epoxide are often much longer than when homogeneous catalysts are used; moreover, prolonged activating pretreatments with hydroperoxide are always necessary before the reaction. The literature cites different hypotheses for this behaviour. Pretreatment is thought necessary to oxidize any Mo^V centre present in the catalyst,^{8,9} and/or to overcome the diffusion barrier between the oxidizing agent and the solid; if this barrier is not overcome, the formation of Mo^{VI} activated centres is hindered.⁸

The present paper reports spectroscopic and spectromagnetic investigations on the 'white isomer' of $MoO_3 \cdot H_2O^{10,11}$ and on its polymer-supported form. Both were tested as catalysts for cyclohexene epoxidation in the heterogeneous phase, and both were subjected to pretreatment with hydroperoxide before the reaction.

EPR, IR and X-ray photoelectron spectroscopic (XPS) investigations allow us to describe the modifications in the metal's electronic structure due to the activating pretreatment with hydroperoxide and to suggest the electronic structure of molybdenum active sites on the catalysts.

Experimental

Materials

 $Na_2MoO_4 \cdot 2H_2O$ (Carlo Erba), Amberlite IR 120 resin (Fluka), H_2O_2 30% v/v (Aldrich), 1,4-dioxane (Aldrich), diethyl ether (Aldrich), ethylbenzene (Aldrich) and anhydrous *tert*-butyl hydroperoxide (*tBHP*; *ca.* 3 mol dm⁻³ in isooctane; Fluka) were used without further purification. Cyclohexene (Aldrich) was distilled before use.

Apparatus

IR spectra were recorded on a Perkin Elmer FTIR 1720 X apparatus; samples were diluted in KBr.

The EPR spectrometer (Varian E-109) was operated in the X band frequency. Spectra were recorded at room temperature on the powdered samples. The g values were determined by standardization with diphenylpicrylhydrazyl (DPPH) and the spin concentration was calculated with a $\pm 10\%$ accuracy by double integration of the resonance lines and referring the area under the absorption curve to that of the standard Varian weak pitch (10^{13} spins cm⁻¹). Care was taken to ensure that the sensitive part of the EPR cavity (1 cm length) was always full; no variations were observed in the apparent density of samples.

The XP spectra were taken in an M-Probe instrument (SSI-Fisons). The source was monochromatic Al-K α radiation (1486.6 eV). The typical pressure in the analysis chamber was 5×10^{-7} Pa. A spot size of 200 mm \times 750 mm and a pass energy of 25 eV, with a resolution of 0.74 eV, were used. The energy scale was calibrated with reference to the 4f_{7/2} level of a freshly evaporated gold sample, taken as 84.00 eV with reference to the 2p_{3/2} level of copper at 932.47 \pm 0.10 eV and the 3s level of copper at 122.39 \pm 0.15 eV.

An electron gun was used in the analysis of insulating samples: a value of 7 eV was mainly used in this work.

Survey analyses were carried out to determine the presence of any particular contaminant: the Mo $3d_{5/2}$ - $3d_{3/2}$ and the C 1s energy regions were explored in detail. The binding energy data of the C 1s region were used as an internal reference at 284.6 eV.

Each measurement was repeated three times and the error in the measurements was ± 0.1 eV, lower than the experimental error usually quoted in the literature for powder samples (+0.2 eV).

Molybdenum determination was accomplished by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Jobin–Yvon 24 Sequential apparatus, equipped with a Czerny–Turner monochromator and a Meinhard pneumatic nebulizer. The analyte line (Mo) was taken at 201.511 nm and the reference line (C) at 139.09 nm.

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X-Ray powder diffraction data were collected in the 2θ region between 5° and 55° on a Siemens D 500 diffractometer, operating with the Bragg–Brentano geometry and with Cu-K α radiation ($\lambda_{\alpha 1} = 1.54056$ and $\lambda_{\alpha 2} = 1.54439$).

Gas-liquid chromatographic (GLC) analyses were performed on a Perkin Elmer Sigma 115 instrument.

Preparation of MoO₃·H₂O

 $Na_2MoO_4 \cdot 2H_2O$ was used as a precursor in two different ways: (i) by dissolving it in a stoichiometric amount of HCl (1 mol dm⁻³); (ii) by ionic exchange on Amberlite IR 120 resin. In both cases, a pale blue powder was obtained after elimination of water. X-Ray diffraction analysis showed that the former product is polycrystalline, while the latter is amorphous. The pattern of peaks of the polycrystalline powder corresponds to that of the 'white molybdic acid' $MoO_3 \cdot H_2O$.^{10,11} The amorphous powder showed identical spectroscopic and spectromagnetic properties (see EPR and XPS investigations), thus it was assumed to be $MoO_3 \cdot H_2O$ and was chosen as the catalyst because of the absence of chlorine impurities.

Treatment of MoO₃·H₂O with H₂O₂

To the aqueous solution of $MoO_3 \cdot H_2O$, a 30% v/v solution of H_2O_2 was added ($H_2O_2 : Mo = 2$). The solution was

stirred at 40 $^{\circ}$ C for 2 h and then dried. A yellow powder was obtained.

Preparation of the Polymeric Support

A carboxylated resin referred to as R1 (Scheme 1) was synthesized by stepwise Michael polyaddition of ethylenediamine-N,N'-diacetic acid to 1,4-bisacryloylpiperazine.¹²

The determination of CO_2H ligand loading was performed as follows: an accurately weighed amount of R1 (1.00 g) was stirred with 30 cm³ of NaOH (0.1 mol dm⁻³). After one night, unreacted NaOH was determined by titration with HCl (0.1 mol dm⁻³). Loading of CO_2H ligands corresponded to 1.081 mmol CO_2H (g resin)⁻¹.

Preparation of Polymer-supported MoO₃ · H₂O

From $MoO_3 \cdot H_2O$ in the Presence of H_2O_2 [MoH₂O₂R1] R1 (0.5 g) was suspended in a 50 cm³ aqueous 1,4-dioxane solution (60% v/v) of $MoO_3 \cdot H_2O$ (1.081 mmol) and H_2O_2 (H_2O_2 : Mo = 2). The slurry was stirred at 40 °C for 2 h, filtered off, washed with distilled water, 1,4-dioxane, diethyl ether and finally dried under vacuum. The samples were yellow.

From $MoO_3 \cdot H_2O$ in the Absence of H_2O_2 [MoR1]

Samples were prepared by the above described procedure, but in the absence of H_2O_2 . Pale blue samples were obtained.



Scheme 1 Synthesis of the R1 resin

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Metal Analysis of Polymer-supported MoO₃·H₂O

An accurately weighed amount of sample (100 mg) was digested in concentrated H_2SO_4 (5 cm³), then concentrated HNO₃ was added dropwise. The resulting limpid solution was made up to 100 cm³ with Milli-Q (Millipore) water. No detectable level of Mo was measured in the water used for dilution. Calibration was performed using molybdenum standard solutions in Milli-Q water. The molybdenum content determined by ICP-AES was in the range 9–12% w/w, corresponding to a CO₂H : Mo molar ratio of *ca.* 1.

Pretreatment with tBHP

Both unsupported samples $(MoO_3 \cdot H_2O)$ and $MoO_3 \cdot H_2O$ treated with H_2O_2) and the supported ones (MoR1 and MoH_2O_2R1) were stirred with *t*BHP in ethylbenzene for 1 h at 80 °C in a 50 cm³ batch reactor. Reaction conditions were: molybdenum, 0.45 mmol; *t*BHP, 9 mmol (*t*BHP : Mo molar ratio = 20); ethylbenzene, 35 cm³.

Cyclohexene Epoxidation

After pretreatment, cyclohexene (20.25 mmol) was added and the mixture was stirred for 1 h at 80 °C. For all samples, the cyclohexene : Mo molar ratio was 45.

Cyclohexene oxide formation was monitored by GLC, withdrawing samples every 5 min in the first 15 min of reaction, then after 30 and 60 min of reaction.

Yields were referred to the amount of tBHP added, *i.e.* 100% yield represented 9 mmol of cyclohexene oxide formed.

Results

Catalytic Activity

Both $MoO_3 \cdot H_2O$ and $MoO_3 \cdot H_2O$ treated with H_2O_2 were tested in cyclohexene epoxidation. Percentage yields of cyclohexene oxide are reported in Fig. 1(*a*) and (*b*). The trends are affected by treatment of the catalyst with H_2O_2 : at the same reaction time yields were always higher for the treated sample. Specifically, the treatment with H_2O_2 minimizes the induction time.

Yields dramatically decrease if reactions are catalysed by polymer-supported molybdenum species: MoR1 was not an active catalyst [Fig. 1(c)], while MoH_2O_2R1 showed weak activity [Fig. 1(d)]. The activating role of treatment with H_2O_2 is thus confirmed.

EPR Investigation

The results of the EPR investigation are summarized in Table 1.



Fig. 1 Yields (%) of cyclohexene oxide for: (a) $MoO_3 \cdot H_2O$, (b) $MoO_3 \cdot H_2O$ treated with H_2O_2 , (c) polymer-supported molybdenum in the absence of H_2O_2 [MoR1] and (d) polymer-supported molybdenum in the presence of H_2O_2 [MoH2O2R1]

$Na_2MoO_4 \cdot 2H_2O$

Pure molybdate used as precursor for $MoO_3 \cdot H_2O$ did not show any resonance line.

 $MoO_3 \cdot H_2O$

 $MoO_3 \cdot H_2O$ obtained by ionic exchange of molybdate on Amberlite showed resonance lines due to a very small amount of Mo^V, coordinated to oxygen in a tetragonally distorted symmetry field¹³ ($g_{\perp} = 1.927$, $g_{\parallel} = 1.890$). The hyperfine nuclear interaction with ^{95,97}Mo was also detectable and could be resolved into six components ($I_{Mo} = 5/2$) ($A_{\perp} = 45$ G, $A_{\parallel} = 80$ G) [Fig. 2(*a*)].

When $MoO_3 \cdot H_2O$ was obtained from $Na_2MoO_4 \cdot 2H_2O$ treated with HCl (1 mol dm⁻³), Mo^V resonance lines were identical to the previous ones. HCl had to be used in a strictly stoichiometric amount, otherwise the shape of the signal showed the presence of molybdenyl chloroanions $MoOCl_n^{m^-}$ (n = 4.5; m = 1.2) ($g_{\perp} = 1.93$, $g_{\parallel} \approx 1.94$).¹⁴

As expected, treatment with H_2O_2 led to the complete disappearance of Mo^V resonance lines [Fig. 2(b)].

Pretreatment with tBHP caused no relevant changes in the nature of the resonance lines.

$MoO_3 \cdot H_2O$ supported on R1 in the Absence of H_2O_2 [MoR1]

These samples had the same spectral behaviour as pure $MoO_3 \cdot H_2O$ [Fig. 2(*a*)], whether $Na_2MoO_4 \cdot 2H_2O$ underwent ionic exchange on Amberlite or was treated with a stoichiometric amount of HCl. However, in the supported samples the amount of MO^V was smaller owing to the dilution of paramagnetic centres with the polymer matrix.

Table 1 EPR data for paramagnetic centres

sample	g_{\perp}	<i>g</i>	A_{\perp}/G	<i>A</i> /G	paramagnetic metal centres (%)
$MoO_3 \cdot H_2O^a$	1.927	1.890	45	80	10-2
MoO ₃ · H ₂ O ^b	1.93	ca. 1.94	n.d.	n.d.	10 ⁻³
$MoO_3 \cdot H_2O^a$ treated with tBHP	1.927	1.890	45	80	10 ⁻²
$MoR1$ (from $MoO_3 \cdot H_2O^a$)	1.927	1.890	45	80	10-4
MoR1 (from $MoO_3 \cdot H_2O^b$)	1.933	1.963	n.d.	75	10-4
MoR1 (from $MoO_3 \cdot H_2O^a$) treated with tBHP	1.927	1.890	45	80	10-4
MoH_2O_2R1 (from $MoO_3 \cdot H_2O^a$) MoH_2O_2R1 (from $MoO_3 \cdot H_2O^a$)	1.927	1.890	n.d.	n.d.	10 ⁻⁵
treated with tBHP	1.927	1.890	n.d.	n.d.	10 ⁻⁵
Mo/SiO ₂ ^c	1.940	1.882	44	98	10 ²

n.d., not detected. ^{*a*} Obtained by ionic exchange on Amberlite IR 120 resin or by acidification with a stoichiometric amount of HCl (1 mol dm^{-3}). ^{*b*} Obtained by acidification with an excess of HCl (1 mol dm^{-3}). ^{*c*} Ref. 13 and 14.

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Fig. 2 EPR spectra, recorded at room temperature, of: (a) $MoO_3 \cdot H_2O$ obtained from $Na_2MoO_4 \cdot 2H_2O$ by ionic exchange on Amberlite IR 120 resin or by acidification with a stoichiometric amount of HCl (1 mol dm⁻³), (b) $MoO_3 \cdot H_2O$ treated with H_2O_2 , (c) MoR1 from $MoO_3 \cdot H_2O$ obtained with an excess of HCl (1 mol dm⁻³) and (d) MoH_2O_2R1

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Note that spectra of supported molybdenum-R1 are similar to those of silica- or alumina-supported molybdenum.^{14,15} The differences in the hyperfine coupling constants are probably due to the better resolution of $Mo/Al_2O_3(SiO_2)$ enriched in ⁹⁵Mo.¹⁴

Samples obtained from Na₂MoO₄ · 2H₂O treated with an excess of HCl show the resonance lines of MoOCl^{m-}_n resolved into six components of hyperfine nuclear interaction with ^{95,97}Mo $[g_{\perp} = 1.933, g_{\parallel} = 1.963, A_{\parallel}(Mo) = 75G]$ and confirm the effect of an excess of HCl on the molybdate [Fig. 2(c)].¹⁴ On this basis, treatment of the molybdate precursor was made by ion exchange on resin in order to avoid the presence of undesired chlorine.

The similarity we found between the EPR spectrum of $MoO_3 \cdot H_2O$ and that of MoR1 suggests that the support does not perturb the Mo^v electronic state and leaves the coordination geometry and the ligand field around the metal unchanged.

The spectrum does not undergo any change after treatment of the catalyst with tBHP.

$MoO_3 \cdot H_2O$ supported on R1 in the Presence of H_2O_2 $[MoH_2O_2R1]$

A very small amount of metal is still present as Mo^{V} [Fig. 2(d)] and corresponds to the form observed on MoR1 (starred lines). This suggests that on supported samples the oxidizing action of H_2O_2 is not as effective as on $MoO_3 \cdot H_2O$.

The strong radical signal at g = 2.003 was found also on R1 treated with H_2O_2 and can very probably be assigned to a peroxyl radical fixed on the resin.

Treatment of the catalyst with tBHP does not cause any change in the nature of the resonance lines with respect to samples before activation.

XPS Investigation

Table 2 summarizes the XPS data. Only hexavalent molybdenum ions were observed, confirming the very low amount of Mo^{v} seen by EPR analysis.

$MoO_3 \cdot H_2O$

Comparison with Na₂MoO₄ \cdot 2H₂O showed that substitution of Na by H led to an increase in the molybdenum binding energies. When MoO₃ \cdot H₂O was prepared by acidification of Na₂MoO₄ \cdot 2H₂O with stoichiometric HCl (1 mol dm⁻³), very small amounts of sodium and chlorine atoms were found during the survey analysis. Unlike in the EPR results, no interactions between chlorine and hexavalent molybdenum were observed. In fact, for the Mo–Cl interaction, the

Table 2 XPS data (in eV)

sample	Mo 3d _{5/2}	Mo 3d _{3/2}
$Na_2MoO_4 \cdot 2H_2O$	231.8	235.0
MoO ₃ ·H ₂ O ⁴	232.7	235.9
$MoO_3 \cdot H_2O^a$ treated with H_2O_2	233.1	236.2
$MoO_{3} \cdot H_{2}O^{a}$ treated with $tBHP$	232.8	236.0
$MoO_3 \cdot H_2O^a$ treated with H_2O_2 and with tBHP	233.0	236.2
MoR1 (from $MoO_3 \cdot H_2O^a$)	232.5	235.6
MoR1 (from $MoO_3 \cdot H_2O^a$) treated with tBHP	232.5	235.8
MoH_2O_2R1 (from $MoO_3 \cdot H_2O^a$) MoH_2O_2R1 (from $MoO_3 \cdot H_2O^a$)	232.6	235.8
treated with tBHP	232.9	236.0

^a Obtained by ionic exchange on Amberlite IR 120 resin or by acidification with a stoichiometric amount of HCl (1 mol dm^{-3}).

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presence of a shoulder in the peak line should be observed. Instead, all peaks were perfectly fitted by a single 100% Gaussian peak.

Treatment of $MoO_3 \cdot H_2O$ with H_2O_2 caused a significant increase in the binding energies.

The changes induced by tBHP on both $MoO_3 \cdot H_2O$ and $MoO_3 \cdot H_2O$ treated with H_2O_2 were negligible.

$MoO_3 \cdot H_2O$ supported in the Absence of H_2O_2 [MoR1]

The sample behaves in a very similar way to $MoO_3 \cdot H_2O$. This suggests that the electronic state of the Mo^{VI} does not change after the supporting process; this is in agreement with the behaviour of Mo^V centres. The small increase in binding energy suggests an electron-donating effect of R1 towards Mo^{VI} .

Treatment with tBHP does not induce any modification in binding energies.

$MoO_3 \cdot H_2O$ supported in the Presence of H_2O_2 [MoH₂O₂R1]

The binding energies show no significant difference between support in the presence and in the absence of H_2O_2 . This behaviour suggests that while unsupported Mo^{VI} centres are strongly affected by treatment with H_2O_2 , those interacting with R1 could not be easily modified by the oxidative treatment. The result agrees with the behaviour of Mo^V centres, which are fully oxidized by H_2O_2 on MoO₃ \cdot H_2O , while on MoH₂O₂R1 few Mo^V centres are still observable.

Treatment with tBHP causes a significant increase in the Mo^{VI} binding energies.

IR Investigation

Analyses performed on $MoO_3 \cdot H_2O$ showed that in the frequency region of Mo=O stretching vibrations, 1000-800 cm^{-1,10} shifts to higher frequencies, together with sharpening of the bands, occurred after treatment with H_2O_2 and *t*BHP [Fig. 3(*a*) and (*d*)]. No relevant differences in the Mo=O vibration energies were observed between MoR1 and MoH₂O₂R1 treated with *t*BHP [Fig. 4(*a*) and (*b*)].

For the IR spectrum of $MoO_3 \cdot H_2O$ treated with H_2O_2 and *t*BHP, significant changes in frequencies were observed



Fig. 3 IR spectra in KBr discs of: (a) $MOO_3 \cdot H_2O$ treated with H_2O_2 and *t*BHP, (b) $MOO_3 \cdot H_2O$ treated with H_2O_2 and *t*BHP and left under IR radiation for 20 min, (c) the same left under IR radiation for 40 min and (d) $MOO_3 \cdot H_2O$



Fig. 4 IR spectra in KBr discs of: (a) MoR1 and (b) MoH_2O_2R1 treated with *t*BHP

with time under IR radiation, in the Mo=O stretching region: after ca. 40 min, the spectrum of yellow $MoO_3 \cdot H_2O$ treated with H_2O_2 and tBHP returned to that of pale blue $MoO_3 \cdot H_2O$ [Fig. 3(a)-(d)]. However, no changes were observed when the corresponding supported sample underwent the same treatment. This behaviour suggests that only unsupported samples are able to interact with KBr.

The results of the IR investigation in the Mo=O stretching frequency region of $MoO_3 \cdot H_2O$ agree with the results obtained by XPS investigation: the increase in Mo=O stretching frequency due to the interaction with H_2O_2 and *t*BHP corresponds to an increase in Mo 3d binding energies. On the other hand, while in R1-supported samples IR investigation shows no perturbing effect by H_2O_2 and *t*BHP on Mo=O frequency, a change of Mo 3d binding energies is observed.

The vibrations observed in the frequency region diagnostic for the coordination mode of the CO_2H group indicate a monodentate behaviour towards molybdenum (1626 and 1440 cm⁻¹).¹⁶ The CO_2H frequencies in R1-supported samples are identical to those in R1 resin.

The comparison between the H_2O bending vibration at *ca*. 1600 cm⁻¹ in $MoO_3 \cdot H_2O$ before and after supporting cannot confirm the substitution of H_2O by CO_2H , because of the overlap with the CO_2H vibrations.

Discussion and Conclusions

In order to clarify why heterogeneous catalysts, unlike the homogeneous ones, need activating pretreatment with hydroperoxide, the electronic structure of molybdenum active sites in $MoO_3 \cdot H_2O$ and in R1-supported $MoO_3 \cdot H_2O$ are discussed in relation to the catalytic activity of these solids.

Both EPR and XPS results show that in $MoO_3 \cdot H_2O$, molybdenum is present almost entirely as Mo^{VI} . The presence of few Mo^V centres implies that there is no need to oxidize this species before reaction with alkenes.

We observed an induction period when the solid was treated only with tBHP, while epoxidation immediately proceeded when $MoO_3 \cdot H_2O$ was also treated with H_2O_2 . Higher Mo 3d binding energies are associated with Mo^{VI} centres treated with H_2O_2 . Thus we conclude that there is a direct relationship between Mo 3d binding energies and the catalytic activity of heterogeneous Mo^{VI} catalysts. This conclusion agrees with the two main mechanisms given for the homogeneous catalytic oxidation of alkenes, due to Sheldon and co-workers¹⁷ and Mimoun.¹⁸ Both suggest the coordination of hydroperoxide to Mo^{VI} as a first reaction step; this leads to an electron-withdrawing effect from Mo^{VI} and to a corresponding increase in the acidic character of the metal centre, both increasing with the oxidation power of peroxide.

The $MoO_3 \cdot H_2O$ interaction with R1 polymeric support is thought to be due to substitution of H_2O by CO_2H , by analogy with substitution products reported for this compound.¹⁰ The location of H₂O on both sides of the double MoO₃ H₂O chains suggests that, in agreement with the experimental $Mo: CO_2H$ molar ratio of 1, MoO_6 octahedra may be completely surrounded and enclosed in the polymer. Substitution of H₂O by CO₂H does not induce the expected large differences in the spectroscopic properties of Mo^{VI} centres; steric hindrance of the coordinated polymeric support does not allow treatment with H₂O₂ and/or tBHP to induce activating electronic changes on much Mo^{vl} . In fact, while Mo binding energies in supported samples show a significant increase after treatment with H2O2 and tBHP, reaction yields in epoxide are very low. It is probable that, as activation involves only surface layers of catalyst, most of the Mo^{VI} is hindered by R1 and could not reach the acidity necessary to become an active site.

Thus, although Mo^{vI} is the oxidation state necessary for catalyst activity, such activity still requires an acidic character of Mo^{vI} centres higher than that found on $MoO_3 \cdot H_2O$.

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