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Electron paramagnetic resonance characterisation of silica-dispersed copper molybdate obtained by sol–gel and impregnation methods

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Silica-dispersed copper molybdates having different Cu : Mo and Cu : Si molar ratios were prepared both by a sol–gel route and a conventional impregnation technique. These materials, used as catalysts for the propene oxidation, were studied in order to assess whether the different preparation methods and/or different Cu : Mo and Cu : Si molar ratios affected the copper(II) coordination. Electron paramagnetic resonance spectroscopy showed that oxo/hydroxo-bridged copper(II) dimers were present in xerogel catalyst precursors and on the surface of fresh impregnated precursor materials, their amount increasing with Cu : Si molar ratio and in impregnated samples. The value of the zero field interaction is very low and decreases with increase in temperature. This means that Cu(II) centres in dimers are spaced fairly far apart and lie in a strongly distorted symmetry field which varies because of the flexible host matrix. Thermal treatment of both xerogels and impregnated samples gave silica-dispersed $Cu_3Mo_2O_9$ catalysts from samples with Cu : Mo molar ratio 1 : 1 and silica-dispersed $CuMoO_4$ from those with Cu : Mo 1 : 2. The presence of polynuclear metal compounds in the crystalline phase seems to be connected to the presence of dimeric species in the precursor. The sol–gel method is more efficient than impregnation to produce catalysts with small and homogeneous particle dimensions of the active phase, for a wide range of Cu : Si molar ratios.

Introduction

Transition metal oxides are currently used as catalysts for hydrocarbon oxidation reactions either as pure compounds or dispersed in a suitable matrix, the latter often being preferred by virtue of decisive improvements in the catalytic properties.[1] This may be due to different factors such as the increase of surface area, the more efficient removal of the heat of reaction from the active sites and the stabilisation of a particular oxide phase, due to strong metal oxide–support interactions. Investigations on metal oxide catalysts supported on a suitable solid medium concerned molybdenum,[2] vanadium[3] and mixed oxides[4] supported on silica or alumina.

Among mixed-metal oxides, metal molybdates play an important role in hydrocarbon oxidation, displaying key properties like strong metal–oxygen bonds and suitable redox couples.[1,5,6] As an example, $Bi_2(MoO_4)_3$ supported alumina is used in the industrial oxidation of propene to acrolein.[7]

Impregnation and coprecipitation techniques have been widely used for the preparation of dispersed oxide catalysts. However, the recent rapid development of the sol–gel processes[8] has provided more effective synthetic procedures.[9] In principle the sol–gel route to heterogeneous catalysts should allow the control of the composition, homogeneity and textural properties of the dispersed systems; this is widely documented in the literature.[10] Nickel and cobalt molybdates dispersed in a silica matrix have been recently prepared by the sol–gel route and tested in the oxidative dehydrogenation of isobutane to isobutene.[11]

The present paper deals with an electron paramagnetic resonance (EPR) study of silica-dispersed copper molybdate, which has been preliminarily tested as a catalyst in the oxidation of propene.[12] Copper molybdates were tested as pure compounds in the oxidation of propene,[13] isobutene[14] and propane;[15] it was suggested that the surface Cu : Mo ratio strongly influences the reaction pathway.[13] Thus, materials having different Cu : Mo and Cu : Si molar ratios and prepared by two synthetic strategies, *i.e.* (i) hydrolysis and condensation of tetramethoxysilane (TMOS) in the presence of Cu(II) and Mo(VI) salt solutions and (ii) impregnation of SiO_2 by Cu(II) and Mo(VI) salt solutions, were considered. The aim was to assess whether different Cu : Mo and Cu : Si molar ratios affect the coordination environment of copper(II) ions and to verify whether the materials obtained by the sol–gel route have different properties from those obtained by the more conventional impregnation technique.

Copper molybdate was chosen both because of its catalytic properties and because copper(II) is a very suitable paramagnetic probe of the catalyst structure.[16–18]

Experimental

Solvents, organic and inorganic compounds were reagent grade and were used as received. Commercial SiO_2 (ICN 32–63) with 200–300 mesh and 200 $m^2\ g^{-1}$ of surface area was used.

Preparation of silica-dispersed copper molybdate by the sol–gel method

$Cu(NO_3)_2{\cdot}3H_2O$ (1.36 mmol) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (with Cu : Mo = 1 : 1 or 1 : 2 molar ratio) were dissolved in water (15 ml), then methanol (2 ml), tetramethoxysilane (TMOS) in different Cu : Si molar ratios (1 : 5, 1 : 10, 1 : 20, 1 : 40), nitric acid 68% w/w (2 ml) and a 0.27 M aqueous solution of NH_4F (1 ml), used as catalyst, were added under magnetic stirring.

Sol–gel transition occurred within 30 min in air at room temperature. Care was taken in order that all samples had the same area of exposed surface (24 cm^2).

Drying of alcogels in air at room temperature went on for 20 days and at last xerogels were obtained.

Xerogels were finely powdered, then heated in an oven at 953 K in air for 20 h. Brown powders were obtained for samples with Cu : Mo : Si = 1 : 1:5, 10, 20, 40 molar ratios and for the sample with Cu : Mo : Si = 1 : 2:40, while for samples with Cu : Mo : Si = 1 : 2:5, 10, 20 green powders were obtained.

Preparation of silica-dispersed copper molybdate by impregnation

The same salts as before, $Cu(NO_3)_2{\cdot}3H_2O$ (5.55 mmol) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Cu : Mo = 1 : 1 molar ratio) were dissolved in water (15 ml), then commercial SiO_2 (Cu : Si = 1 : 5, 1 : 10, 1 : 20, 1 : 40 molar ratio) was added under magnetic stirring. After contact for 15 min, the slurry was dried *in vacuo* at 363 K for *ca.* 2 h, until a fine green powder was obtained. Then, the material was heated in an oven at 953 K for 20 h, obtaining a brown powder.

Apparatus

EPR spectra were recorded at the X-band frequency on a Bruker EMX EPR spectrometer, equipped with a variable temperature unit BVT 2000 (Bruker). Unless otherwise indicated, a modulation frequency of 100 kHz, modulation amplitude of 16 G, microwave power of 5 mW and temperature of 123 K were used. The *g* values were determined by standardisation with diphenylpicrylhydrazyl (DPPH) and the spin concentration was calculated by double integration of the resonance lines and referring the area under the absorption curve to that of the standard Bruker weak pitch ($9.7 \times 10^{12} \pm 5\%$ 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.

X-Ray diffraction (XRD) spectra were obtained by a Philips PW 1050 instrument using Cu-Kα radiation. The crystallite mean size was estimated from the diffraction peak widths using the Debye–Scherrer equation. Energy dispersive X-ray microanalyses (EDX) were performed by the SEM equipment JEOL 6400 EDS Tracor. BET surface areas were measured using a Micromeritics instrument.

Results

Silica-dispersed copper molybdate by the sol–gel method

Precursor solutions and alcogels. In order to follow the changes in Cu(II) environment during the sol–gel process, EPR spectra were recorded on samples drawn immediately after the addition of water, methanol, TMOS, nitric acid and ammonium fluoride in sequence to three batches containing: (i) copper nitrate, (ii) ammonium heptamolybdate and (iii) the two salts together. The amounts of reagents were the same as those reported in the experimental section for the preparation of catalysts. Spectra are shown in Fig. 1.

(i) The spectrum of $Cu(NO_3)_2$ frozen solution in water showed an unresolved broad isotropic signal ($g = 2.17$; magnitude *ca.* 10^{18} spins cm^{-1}) due to the segregation of ice and copper salt crystals, which induces coupling of the paramagnetic Cu(II) centres.[18]

As expected, the addition of methanol (H_2O/MeOH = 7.5 v/v) produced, upon cooling, a glassy matrix which gave well resolved signals of magnetically diluted copper(II) ions. The values of *g* and *A* tensor components ($g_{\parallel} = 2.42$, $g_{\perp} = 2.09$, $A_{\parallel} = 115.0$ G) are consistent with those of copper(II) complexes in a tetragonal symmetry field of oxygen atoms.[19] The starred signal in Fig. 1 is attributable to the interaction of two copper centres (see below) and was absent in a ten times more diluted water–methanol solution. Double integration of the resonance lines showed the presence of *ca.* 10^{19} spins cm^{-1}.

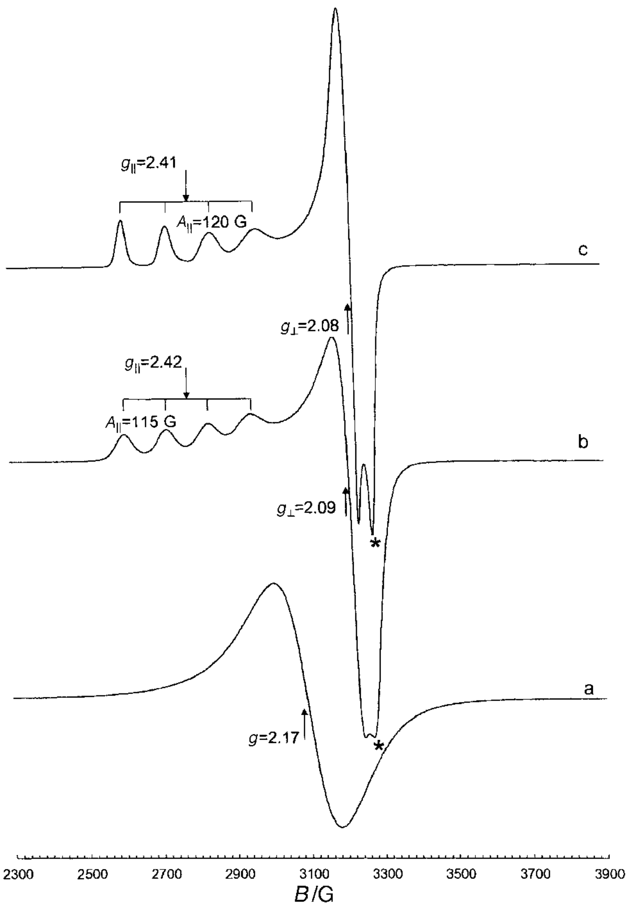

Fig. 1 EPR spectra recorded at 123 K of (a) a water solution of $Cu(NO_3)_2$. The same solution after the addition in sequence of (b) methanol and TMOS (molar ratio Cu : Si = 1 : 20) and (c) nitric acid and ammonium fluoride. EPR spectra are also the same in the presence of ammonium heptamolybdate. Starred lines indicate coupled copper centres.

The addition of TMOS led to no variation in either the spectrum or the phase of sample, which remained a limpid blue solution [resembling aqueous $Cu(NO_3)_2$].

After addition of HNO_3, the spectrum (magnitude *ca.* 10^{18} spins cm^{-1}) showed a very slight decrease in $g_{\parallel}$ and an increase in $A_{\parallel}$ values ($g_{\parallel} = 2.41$, $g_{\perp} = 2.08$, $A_{\parallel} = 120.0$ G). The variations are very small and could be tentatively attributed both to a decrease in Cu(II) positive charge[19] and/or to an increase in tetragonal distortion of the symmetry field,[18] due to partial substitution of H_2O by NO_3^-.[20]

By addition of NH_4F, used as catalyst, a gel formed within 1 h, but the magnetic parameters remained unchanged.

(ii) With ammonium molybdate alone, silent EPR spectra indicated the absence of paramagnetic species.

(iii) The two salts together (Cu : Mo = 1 : 1 molar ratio) showed EPR signals very similar to those observed with $Cu(NO_3)_2$ alone. In this case, the addition of TMOS caused the immediate precipitation of a white amorphous solid, however the EPR spectrum was the same as before TMOS addition ($g_{\parallel} = 2.42$, $g_{\perp} = 2.08$, $A_{\parallel} = 115.0$ G). This precipitate, analysed by EDX, gave a Cu : Mo : Si molar ratio of 1 : 1 : 4.

Acidification with HNO_3 induced changes in the EPR spectrum similar to those observed with $Cu(NO_3)_2$ ($g_{\parallel} = 2.41$, $g_{\perp} = 2.08$, $A_{\parallel} = 120.0$ G), and the precipitate completely dissolved.

After the addition of NH_4F, the magnetic parameters were the same as for $Cu(NO_3)_2$, but in this case a gel formed within 30 min. These results suggest that the alcogel formation, catalysed by NH_4F, is further favoured in the presence of $(NH_4)_6Mo_7O_{24}$.

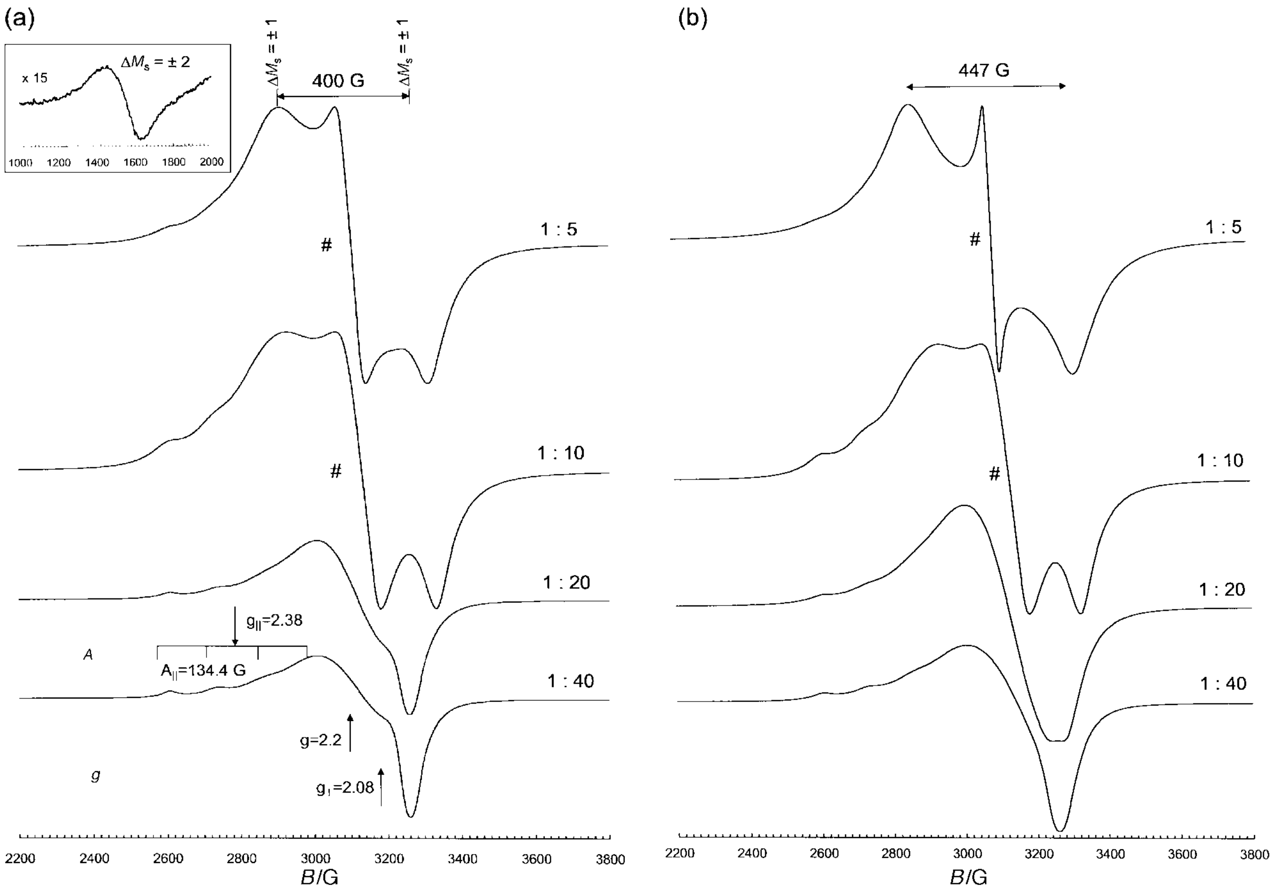

Fig. 2 (a) EPR spectra recorded at 123 K of xerogels (Cu : Mo = 1 : 1 molar ratio) with different Cu : Si molar ratios dried for 20 days. The insert shows the $\Delta M_s = \pm 2$ transition of the Cu : Si = 1 : 5 molar ratio sample; (b) EPR spectra recorded at 123 K of samples obtained by impregnation technique (Cu : Mo = 1 : 1 molar ratio) with different Cu : Si molar ratios. Cu : Si molar ratios are reported on the right side of the spectra. The symbol # indicates the double quantum transition line.

Xerogels

In order to study the change in copper coordination due to the alcogel-xerogel transition and to test the influence of different Cu : Mo and Cu : Si molar ratios on the copper environment, alcogels were prepared by using Cu : Mo = 1 : 1, 1 : 2 and Cu : Si = 1 : 5, 1 : 10, 1 : 20, 1 : 40 molar ratios; then they were dried for 20 days, ground and submitted to EPR analysis [Fig. 2(a)]. From now on these samples will be referred to as xerogels.

The EPR spectra of xerogels with Cu : Mo : Si = 1 : 1 : 40, 1 : 1 : 20 molar ratios showed the resonance lines of the $S = 1/2$ copper(II) ions in tetragonal symmetry of four oxygens ($g_\parallel = 2.38$, $g_\perp = 2.08$, $A_\parallel = 134.4$ G). The differences in the Cu(II) magnetic parameters with respect to alcogels suggest that the xerogel formation caused an increase in tetragonal distortion[18] and/or a decrease in Cu(II) positive charge.[19]

An isotropic broad resonance at $g \approx 2.2$ was also observed, whose intensity is higher in the sample with Cu : Si = 1 : 20 molar ratio.

The more concentrated samples, having Cu : Mo : Si = 1 : 1 : 10 and 1 : 1 : 5 molar ratios, at 123 K showed strong signals superimposed to the resonance lines of the $S = 1/2$ copper(II) ions previously described, which are attributable to EPR active species with $S > 1/2$. These lines are due to the $\Delta M_s = \pm 1$ transitions [Fig. 2(a)] of a Cu(II) dimeric species, with small values of the zero-field splitting parameters.[21] In fact, the $\Delta M_s = \pm 2$ half-field transition [Fig. 2(a) insert] showed very low intensities. Spectra are poorly resolved and it is difficult to understand whether the axial symmetry of the isolated Cu(II) centres is kept in dimers. However, in the hypothesis that the symmetry of the dimeric species is not strongly different from the axial one, the distance between the two $\Delta M_s = \pm 1$ peaks indicated in Fig. 2(a), 400 G, gives a zero-field splitting value, D, of 0.019 cm^{-1}.[22] The zero-field interaction is about the same in samples with Cu : Mo : Si = 1 : 1 : 10 and 1 : 1 : 5, but the resonances of the isolated monomeric Cu(II) centres are better detectable in the less concentrated sample.

The signal indicated by the symbol # was not observed at microwave powers lower than 5 mW. On these grounds, it is attributable to a double quantum transition and confirms the presence of the $S = 1$ spin state.

Whatever Cu : Si molar ratios were used, the areas under the absorption curves corresponded to the presence of *ca.* 10^{19} spins cm^{-1}.

Strong reversible variations were observed recording spectra of the most concentrated sample with Cu : Mo : Si = 1 : 1 : 5 molar ratio at different temperatures (Fig. 3). Spectra could not be recorded at room temperature, probably because of the large amount of polar molecules (H_2O and CH_3OH) still present in xerogels. At 223 K a broad symmetric resonance became visible which, from 203 K, took a shape similar to that of dimeric species with $S = 1$ spin state. From 203 K a narrow resonance at $g = 2.16$ became detectable, which is attributable to a double quantum transition.[23]

The value of the zero-field parameter significantly varied with temperature and, though the lack of resolution hindered us from distinguishing the fine structure of the spectrum, an increase of about 70% in D' was observed from 203 to 100 K (Fig. 3). The differences were not unexpected; in fact the major contribution to the zero-field parameter for transition metal compounds comes from the mixing of the ground triplet state

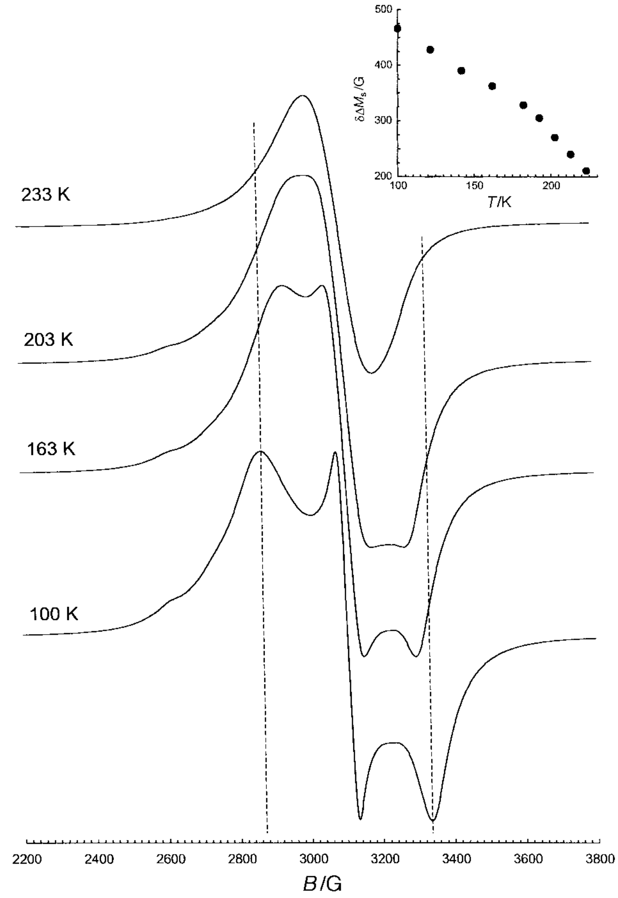

Fig. 3 EPR spectra recorded at different temperatures of a xerogel (Cu : Mo : Si = 1 : 1 : 5 molar ratio) dried for 20 days. Vertical lines highlight the increasing spread of $\Delta M_s = \pm 1$ resonances. The insert reports the trend of $\delta\Delta M_s$ *vs.* temperature (range 100–203 K), where $\delta\Delta M_s$ is the distance between the $\Delta M_s = \pm 1$ resonances.

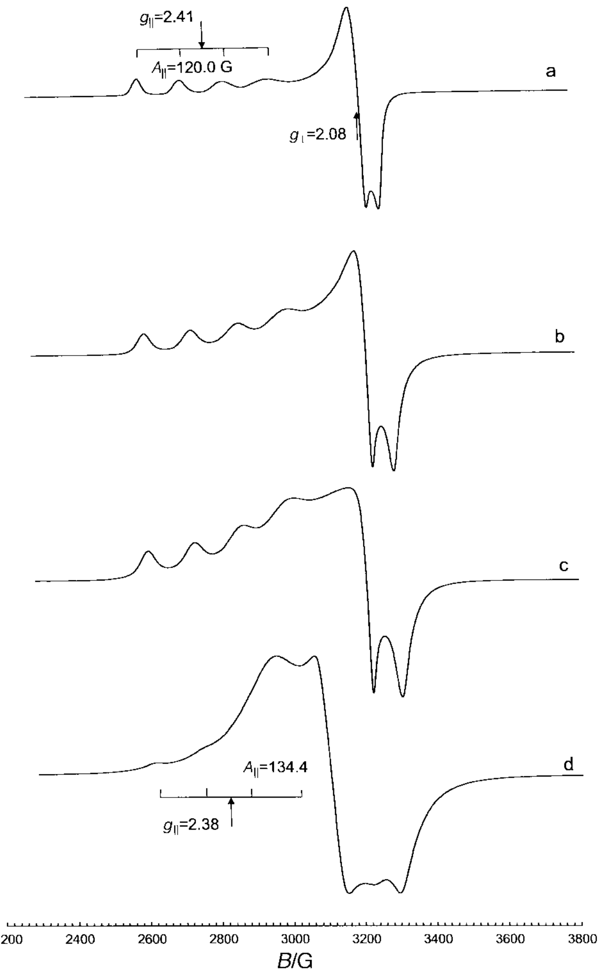

Fig. 4 EPR spectra of a xerogel (Cu : Mo : Si = 1 : 1 : 10 molar ratio) during the drying process: (a) just after the gel formation and after (b) 7, c) 15 and (d) 20 days.

with the excited ones through the spin–orbit coupling interaction.[24] Temperature variations can induce strong structural changes in a flexible host like xerogel, producing changes in the energy difference between the ground and the excited Cu(II) triplet states. In our case the decrease in temperature induces a stronger mixing among the spin–orbit coupled triplet energy levels.[24]

The variation of the spectra with temperature also indicates that the $g_\parallel$ value increased with decreasing temperature. This suggests that the tetragonal distortion is less pronounced at low temperatures, in agreement with the stronger mixing among the spin-orbit coupled energy levels deduced from the D' variations.

The changes in copper coordination environment during the drying of alcogels were monitored by EPR spectroscopy. Spectra of the sample with Cu : Mo : Si = 1 : 1 : 10 molar ratio showed that copper centres, which were magnetically diluted after the addition of NH_4F, with time approached each other giving rise to dimeric species (Fig. 4). The uncoupled species varied the magnetic parameters: from those observed after the addition of NH_4F ($g_\parallel = 2.41$, $g_\perp = 2.08$, $A_\parallel = 120.0$ G) to the values observed on xerogel after 20 days ($g_\parallel = 2.38$, $g_\perp = 2.08$, $A_\parallel = 134.4$ G).

Samples with Cu : Mo = 1 : 2 and Cu : Si = 1 : 5, 1 : 10, 1 : 20, 1 : 40 molar ratios were also studied. No relevant variations due to the difference in molybdenum amount were observed.

Thermally treated xerogels

After thermal treatment at 953 K, samples with different compositions (Cu : Mo = 1 : 1, 1 : 2 and Cu : Si = 1 : 5, 1 : 10, 1 : 20, 1 : 40) underwent EPR and XRD investigations.

EPR spectra of samples with Cu : Mo = 1 : 1, whatever the Cu : Si molar ratio, showed the resonance lines of $S = 1/2$ copper(II) ions superimposed by isotropic broad lines at $g \approx 2.2$. No dimers with detectable difference in $\Delta M_s = \pm 1$ transitions were evident. Signal intensities decreased with increasing Cu(II) concentration.

The total amount of paramagnetic copper(II) centres considerably decreased (> 10 times) in comparison with the xerogel precursors.

A very weak signal due to Mo(V) in a tetragonally distorted symmetry field ($g_\perp = 1.92$, $g_\parallel = 1.88$)[25] was observed in all spectra.

In all samples, XRD spectra assessed the presence of $Cu_3Mo_2O_9$ crystallites,[26] responsible for the brown colour of samples, all having a similar mean size with the exception of those with Cu : Si = 1 : 5 molar ratio (Table 1). The ratio between the crystalline and amorphous phase increased with copper concentration (Fig. 5).

Samples with Cu : Mo = 1 : 2 molar ratio showed EPR signals similar to those observed with Cu : Mo = 1 : 1 molar ratio and had the same intensity trend, but they were less intense. In this case the signal intensity decreased more than twenty times in comparison with the xerogel precursors.

In green samples with Cu : Si = 1 : 5, 1 : 10, 1 : 20 molar ratios XRD spectra assessed the presence of $CuMoO_4$ crystallites[27] while the brown sample with Cu : Si = 1 : 40 formed the $Cu_3Mo_2O_9$ phase. Thus the sample colour is strictly connected with the crystalline phase. Crystallites had a similar mean size at each Cu : Si ratio (Table 1). It is important to observe that EDX measurements performed on samples obtained from

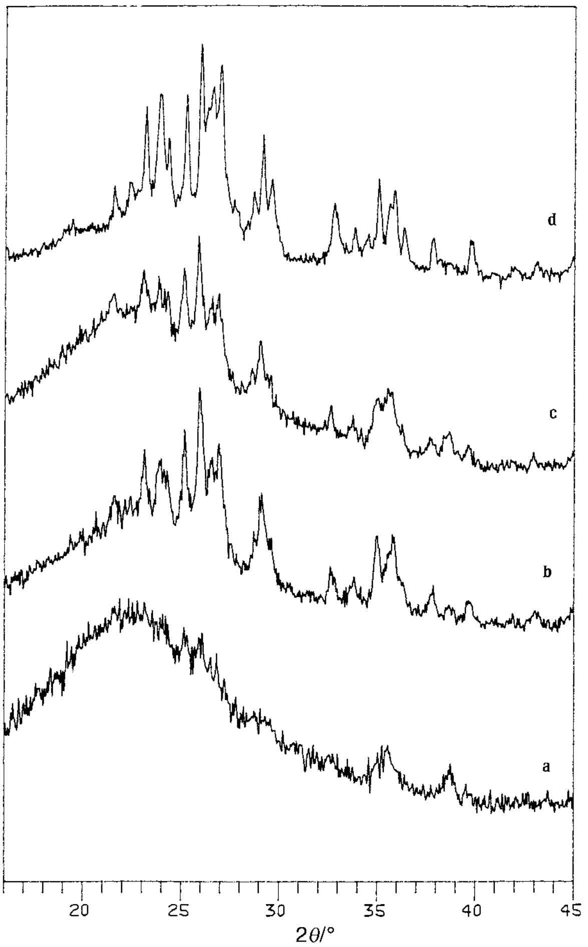

Fig. 5 XRD spectra of $Cu_3Mo_2O_9$ crystalline phase in thermally treated xerogels (Cu : Mo = 1 : 1 molar ratio) with different Cu : Si molar ratios: (a) 1 : 40; (b) 1 : 20; (c) 1 : 10; (d) 1 : 5.

Table 1 Estimated crystallite mean sizes (nm)

Preparation method	Cu : Mo (mol/mol)	Crystalline phase	Cu : Si (mol/mol)			
			1 : 5	1 : 10	1 : 20	1 : 40
Sol–gel	1 : 1	$Cu_3Mo_2O_9$	48	32	37	n.d.[a]
	1 : 2	$CuMoO_4$	28	31	32	n.d.[a,b]
Impregnation	1 : 1	$Cu_3Mo_2O_9$	61	54	36	n.d.[a]

[a] n.d.-not determined. [b] $Cu_3Mo_2O_9$.

precursors with Cu : Mo = 1 : 2 molar ratio gave the same value, 1 : 2, of Cu : Mo molar ratio in the final products. Since the crystalline phase is $CuMoO_4$, it could be suggested that not all molybdate anions were available for the formation of mixed oxide phases, being probably employed to form silicomolybdate host species.

The surface area measurement tested on a sample having Cu : Mo : Si = 1 : 2 : 20 molar ratio, gave a value of 330 $m^2\,g^{-1}$, significantly lower than the value (430 $m^2\,g^{-1}$) observed for a pure silica gel treated under the same conditions. This result was expected, because of the presence of the crystalline phase.

Silica-dispersed copper molybdate by impregnation

Samples prepared by the impregnation technique with Cu : Mo = 1 : 1 and Cu : Si = 1 : 5, 1 : 10, 1 : 20 and 1 : 40 molar ratios were investigated.

EPR spectra showed the same type of signals as xerogels at each Cu : Si ratio [Fig. 2(b)]. Also in this case the absolute amounts of paramagnetic species were *ca.* 10^{19} spins cm^{-1}; the relative amounts of the isolated and coupled copper centres varied with copper concentration, giving an amount of the coupled species increasing with Cu : Si molar ratio.

In the more diluted samples (Cu : Si = 1 : 40, 1 : 20 molar ratio) the broad band at $g \approx 2.2$ was present in larger amounts than in xerogel samples with the same composition. This suggests this band is due to a spin interaction between copper centres, which is reasonably higher in impregnated samples.

In concentrated samples (Cu : Si = 1 : 10, 1 : 5 molar ratio), triplet state lines were evident. The zero-field parameter significantly increased by doubling the copper content [Fig. 2(b)] and in the 1 : 1 : 5 sample it was higher than in the xerogel with the same composition [Fig. 2(a)].

Thermally treated samples

After thermal treatment at 953 K, impregnated samples showed the same EPR spectra as the corresponding samples from xerogels.

The intensity trend was also the same as before, but in this case the intensities were lower than those of samples from xerogels having Cu : Mo = 1 : 1 molar ratio.

The total amount of copper(II) considerably decreased (more than thirty times) in comparison with the corresponding impregnated precursors.

XRD spectra on all these brown samples showed the presence of $Cu_3Mo_2O_9$ crystallites. Both the crystallite mean size and the ratio between crystalline and amorphous phases gradually increased with copper concentration; the crystallite mean size of the more concentrated samples (Cu : Si = 1 : 10, 1 : 5) was significantly higher than in sol–gel materials (Table 1).

Discussion

The investigation performed on the precursor solutions showed that the presence of $(NH_4)_6Mo_7O_{24}$ promotes the gelation process. This can be due to $[MoO_4]^{2-}$ species, coming from the shift of the equilibrium $[Mo_7O_{24}]^{6-} + 4H_2O \rightleftharpoons 7[MoO_4]^{2-} + 8H^+$ in aqueous solution; $[MoO_4]^{2-}$ probably attacks the electrophilic silicon centre of TMOS, as well as the F^- catalyst, leading to the formation of a silicomolybdate framework. Actually addition of TMOS to a water–methanol solution of $Cu(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ gave a precipitate containing copper, molybdenum and silicon in atomic ratio 1 : 1 : 4 (from EDX measurements), suggesting an active role of molybdenum in the host matrix formation. Moreover, EDX measurements performed on the thermally treated xerogels with Cu : Mo = 1 : 2 molar ratio (where the detected crystalline phase is $CuMoO_4$) confirmed the overall 1 : 2 ratio and again suggested the incorporation of significant amounts of molybdenum in the host matrix.

EPR data showed that the environment of copper centres in alcogels is not affected by the host centres. Thus copper centres should be trapped in the alcogel host, but the interaction with the framework is probably hindered by the surrounding solvent molecules.

The drying of alcogel causes a slow removal of the solvent molecules and a condensation of aquo and hydroxo groups of both silica and copper centres. This probably leads to the grafting of copper on silica *via* oxo and hydroxo groups. In fact the EPR data indicated that during the alcogel–xerogel transition both the positive charge of the magnetically diluted Cu^{2+} centres decreases and the tetragonal distortion increases.

The interaction of copper centres *via* bridging oxo and hydroxo groups causes the spin coupling effects observed in xerogel samples. At the lower copper contents the copper–copper interaction was assessed by the presence of the broad band at $g \approx 2.2$. As the copper content increases, dimeric interactions become evident. The values of the zero-field parameters are very low, suggesting both low dipolar contribution and low spin–orbit coupling effects. This means that Cu^{2+} centres are largely spaced and lie in a strongly distorted symmetry field.[24] An increase in D' value of *ca.* 70% (Fig. 3) was observed by decreasing the temperature from 203 to 100 K; this appears a very large variation if compared with that very recently reported by Higgs *et al.*[28] for a dimeric Cu(II) compound (about 10%), but it is in agreement with an easier conformational change of two Cu^{2+} centres that lie in a flexible host like xerogel, rather than a crystal lattice.

At 233 K (Fig. 3) the two $\Delta M_s = \pm 1$ transitions cannot be distinguished because of the very low value of the D' parameter. This suggests that the isotropic broad signal at $g \approx 2.2$ seen in less concentrated samples is mainly due to widely separated Cu(II) centres.

Interactions among copper(II) ions were observed also in samples obtained by impregnation of SiO_2. The trend of the spin–spin coupling interaction between the metal centres is the same as for xerogels. However in comparison with xerogels, impregnated samples show a higher amount of coupled Cu(II) ions in the more diluted samples (Cu : Si = 1 : 20, 1 : 40 molar ratios), and a higher D' value in the most concentrated sample (Cu : Si = 1 : 5 molar ratio). The increase in D' value is more probably due to an increase in the dipolar contribution than to a decrease in distortion; this agrees also with the larger dimension of crystallites obtained by thermal treatment of impregnated samples in comparison with xerogels (Table 1).

In a recent paper Klonkowski *et al.*[16] attributed the isotropic broad signal to copper complexes of the type $[CuR_6]^{2+}$ (where R is H_2O and/or CH_3OH) undergoing free rotation within the pores of the silica gel. They excluded coupling among copper ions. Our results show that the broad band at $g \approx 2.2$ was also observable at 123 K, where the rotation within silica pores should not be reliable. Moreover rotation effects should be more efficient in xerogels than in impregnated samples, while the spectra of xerogels showed a less intense band at $g \approx 2.2$. Finally, within the coupling hypothesis, the presence of dimers with a well detectable D' parameter at the highest copper concentration seems to be the consequence of a reduction in separation between the interacting copper centres.

All thermally treated samples showed very small amounts both of isolated and coupled Cu(II). Possible explanations for the decrease of paramagnetic copper(II) centres, from ten to thirty times the amount in samples before thermal treatment, could be in principle: (i) a lower density of the catalyst, (ii) a partial reduction of Cu(II) to Cu(I) or (iii) an EPR silent copper–copper magnetic coupling. The first hypothesis can be excluded, as thermal treatment increases the density. On the other hand, oxidative conditions make copper(II) ion reduction unlikely, while the formation of amorphous CuO and its decomposition to Cu_2O can be excluded since CuO decomposes above 1073 K.[29] Since the signals of dimeric species with detectable D' are present before thermal treatment of samples, but were not observed in thermally treated samples, a reasonable hypothesis is that the dimeric species are precursors of EPR silent coupled copper(II) species.

The higher amount of coupled species observed in impregnated samples is in accord with the lower intensity of the EPR spectra of the corresponding thermally treated samples.

The Cu : Si molar ratio affects both the degree of crystallisation and the crystallite dimensions (Fig. 5 and Table 1), but in catalysts obtained by impregnation the changes in dimensions are larger than in those from xerogel samples. The sol–gel method leads to metal dispersed solids with an almost constant size of $Cu_3Mo_2O_9$ crystallites.

The Cu : Mo molar ratio also has an effect on the nature of the crystalline phase: $CuMoO_4$ was obtained rather than $Cu_3Mo_2O_9$ for Cu : Mo = 1 : 2 molar ratio; it appears that more molybdenum is consumed than is found in the crystalline product, in agreement with the role of Mo in the host matrix formation. In addition, high amounts of SiO_2, as in the Cu : Mo = 1 : 40 molar ratio sample, lower the molybdenum available for crystalline phase formation, as in $Cu_3Mo_2O_9$.

These results suggest that both in xerogels and on the surface of impregnated catalysts, the coupling of copper centres occurred through the formation of oxo/hydroxo-bridged copper dimers.

These are more likely as precursors of the polynuclear metal compounds obtained in the crystalline phase ($Cu_3Mo_2O_9$ or $CuMoO_4$).

Conclusions

The sol–gel method seems to be superior to impregnation in producing catalysts with small and homogeneous particle dimensions of the active phase and the dispersion of the catalyst precursors in the silica gel hindered particle growth with increasing copper concentration over a wide range of Cu : Si molar ratios.

The catalytic activity in the propene oxidation of some thermally treated xerogels was compared with that of impregnated catalysts having the same Cu : Mo : Si molar ratios. In each case, the sol–gel catalysts promoted a higher conversion than the impregnated ones.[12]

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