

## Formation of copper-based particles trapped in a silica xerogel matrix

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Using IR absorption and X-Ray diffraction we have analyzed the incorporation of Cu-based aggregates in a SiO<sub>2</sub> matrix in samples prepared by the sol-gel method. We doped the silica xerogels samples using two different copper sources: Cu(NO<sub>3</sub>)<sub>2</sub>•2.5H<sub>2</sub>O and copper particles chemically synthesized. The samples were studied as a function of annealing temperature. It is found that by heat treatment and the appropriate copper precursor we can produce particles of metallic Cu, cuprous and cupric oxide. The obtained IR absorption results allow studying the interaction of the metal-based species and the oxide support.

*Keywords:* Sol-gel; infrared spectroscopy; X rays; structure; glasses

### 1. Introduction

Among the many applications of glass-metal composites, one of the most important is as catalysts. Silica-supported copper catalysts have been reported as excellent catalysts in the NO reduction [1-3]. Stabilization of the active phase in supported catalysts depends on the support and its preparation method; among the preparation methods the sol-gel technique offers some advantages. With this preparation method copper species are effectively uniformly incorporated into the ionic oxide network [4,5] and may lead to more stable catalysts than those prepared by conventional methods. The sol-gel polymerization of the metal alkoxides in the presence of inorganic salts leads to the formation of ceramic oxide materials that exhibit important microstructure properties [6].

The main aim of this work is to explore the microstructure of the support material (glass) and the evolution of the metallic species in the glass network under heat treatments. Silica xerogels were prepared by the sol-gel route and annealed at different temperatures. In order to get powder samples, gels were ground after the annealing. The samples were used to obtain information about the structural modifications, at molecular level, induced by the doping element and the heat treatments, and mainly to understand the metal species evolution as well as metal-glass interaction. Silica xerogel samples were doped using two different copper precursors: copper nitrate

and copper particles chemically synthesized. Amounts of copper nitrate and copper particles were determined in order to obtain final silica glasses of CuO-SiO<sub>2</sub> and Cu-SiO<sub>2</sub> with concentrations of the doping element of 30 wt. %.

### 2. Experimental methods

The starting solutions, for the silica xerogels, were prepared by mixing tetraethyl orthosilicate (TEOS), water and ethanol. The mole ratios of ethanol to TEOS and water to TEOS were 4:1 and 11.67:1, respectively. In both sets of samples, the concentration of copper precursors was calculated to obtain 30 wt.% of metal species. To catalyze the hydrolysis/condensation reaction 0.034 moles of HNO<sub>3</sub> were added for mole of TEOS.

The nitrates used for the addition of copper were Cu(NO<sub>3</sub>)<sub>2</sub>•2.5H<sub>2</sub>O, the metal nitrate was dissolved in water and separately the TEOS and ethanol were also mixed, then a homogeneous solution of all components was obtained by mixing them for about 15 minutes using a magnetic stirrer.

The copper particles were obtained using a water-oil microemulsion and using NaBH<sub>4</sub> as the reducing agent. Microemulsions were prepared by solubilizing aqueous CuCl<sub>2</sub> or NaBH<sub>4</sub> solutions into a TX-100 surfactant/hexanol/hexane solution. The CuCl<sub>2</sub> was solubilized in one solution and the NaBH<sub>4</sub> in other solution, where the salt concentrations in the aqueous

phases were 0.1M in  $\text{CuCl}_2$  and 0.3 in  $\text{NaBH}_4$  respectively [7].

The preparation of copper particles was achieved by mixing rapidly the same volume of each water/microemulsion. Depending on the water/microemulsion ratio and the pH of the  $\text{CuCl}_2$  solution, the amount of  $\text{Cu}_2\text{O}$  present in the Cu particles can vary drastically. In the present case, the copper particles were made at room temperature without removing the oxygen. The final amount of  $\text{Cu}_2\text{O}$  measured on the Cu particles by X-ray diffraction, not showed in this work, indicated the presence of less than 4 wt % of the oxide. The  $\text{Cu}_2\text{O}/\text{Cu}$  wt% was determined by the relative intensities of the main X-ray corresponding reflexion peaks [8]. For the particle doped xerogels, they were mixed with ethanol directly to the homogenous TEOS: $\text{H}_2\text{O}$  solution, and the final solution was obtained mixing by them for about 15 minutes using a magnetic stirrer. The two solutions were placed in a container in a constant temperature bath at  $35^\circ\text{C}$ .

The samples were named set A for the nitrate copper case and set B for the particles one. In both sets of samples, soft pieces of glass were obtained after about 48 hr, previously, the bath temperature was fixed at  $50^\circ\text{C}$  during 2 hr. The solution were heated in an oven in air atmospheric at about  $100^\circ\text{C}$  to produced a rapid dried of the solution and therefore the gelation was accelerated; at about one hour the solution was completely dried and solid.

For subsequent annealing the samples were introduced in the oven at the desired temperature for 25 minutes at atmospheric air conditions. Those pieces were grounded to form a fine powder.

The Infrared (IR) spectra were measured in a FT-IR spectrometer Nicolet System model Avatar using the diffuse reflectance (DR) mode, for which 0.05 gr. of powder sample were mixed with 0.3 gr. of KBr. The X-ray diffraction patterns were obtained in a Rigaku 2200 diffractometer using  $\text{CuK}_\alpha$  radiation ( $\lambda=1.54\text{\AA}$ ).

## Results

Fig. 1 and Fig. 2 show the IR absorption spectra in the range of 400 to  $2200\text{ cm}^{-1}$  for  $70\text{SiO}_2:30\text{CuO}$  and  $70\text{SiO}_2:30\text{Cu}$  powdered samples. Each of the three major features related to Transversal Optical (TO) absorption bands shown in the figures can be characterized in terms of a particular vibration mode of the oxygen (O) atom respect to the silicon (Si) atom which they bridge. Rocking (R) of the O atom about an axis through the two Si atoms characterize the vibrational behavior of the lowest-frequency TO band centered at  $\approx 457\text{ cm}^{-1}$ . Bending (B) of the O atom along a line bisecting the axis formed by the two Si atoms characterizes the vibrational mode of the middle TO band centered at  $\approx 800\text{ cm}^{-1}$ .

The remaining TO band and his high-frequency

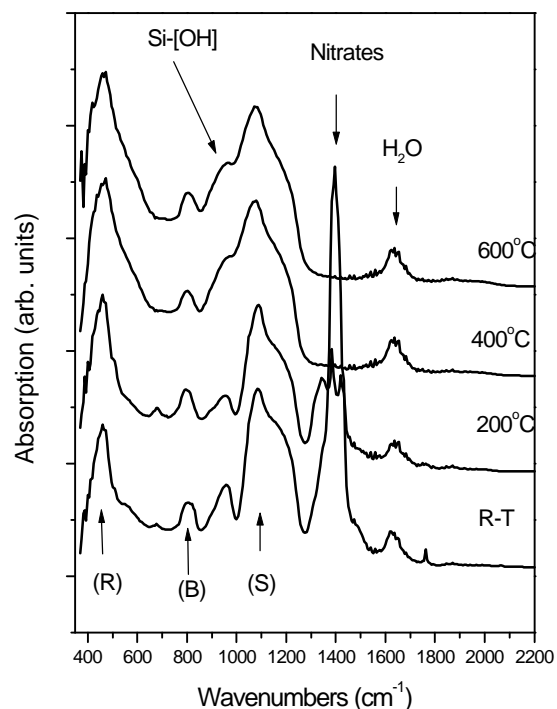


Figure 1 IR absorption spectra in the range of 400 to  $2200\text{ cm}^{-1}$  for  $70\text{SiO}_2:30\text{CuO}$  powdered samples

shoulder are due to an asymmetrical stretch (S) motion in which the O atom moves back and forth along a line parallel to the axis through the two Si atoms [9,10].

The main band of the  $\text{SiO}_2$  IR spectra is the corresponding to the asymmetric stretching (S) mode at  $1078\text{ cm}^{-1}$ , however its presence at  $1150\text{--}1300$  it is not clear. In previous work it has been reported the IR spectra in which a shoulder, in the frequency range of  $1150$  to  $1250\text{ cm}^{-1}$ , has an amplitude comparable or bigger than the main stretching band at  $1076\text{ cm}^{-1}$  [11,12]. This has been achieved in vitreous  $\text{SiO}_2$  samples prepared by the sol-gel method using specific preparation conditions. From Figure 1 and 2 we can see that the bending (B) bands, in both set of samples, suffer slight modifications according to the annealing temperature. While the rocking (R) bands shows a noticeable increment in its relative intensity, respect to the main (S) band, this fact is more pronounced in the set of samples A. It has been reported that the Cu-O vibration in cupric oxide has IR active modes at 420, 425, and  $528\text{ cm}^{-1}$  [13], then the relative increment of the intensity of the (R) band could be consequence of overlapping of the (R) band and the Cu-O bands. For the spectra corresponding to the B samples there is an additional band at about  $620\text{ cm}^{-1}$ , this band corresponds to vibrational modes of Cu-O in  $\text{Cu}_2\text{O}$  phase [14]. Also from the figures 1 and 2, we can observe a band at  $\approx 950\text{ cm}^{-1}$  assigned to the vibration of the Si-[OH] groups [15]; this band shows a noticeable evolution and changes with the annealing temperature. The Si-O

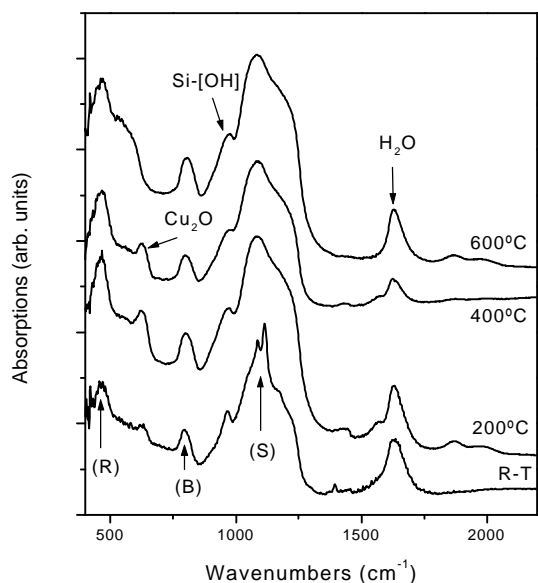


Figure 2 IR absorption spectra in the range of 400 to 2200 cm<sup>-1</sup> for 70SiO<sub>2</sub>:30Cu powdered samples

stretching (S) band at ~1078cm<sup>-1</sup> seems to suffer modifications with temperature, as expected due to densification. There are two additional bands at ~1450 cm<sup>-1</sup> and ~1650 cm<sup>-1</sup>, these bands are related to the nitrate groups and “free” molecular water vibrations, respectively [16]. For the set of samples A, the band assigned to the nitrate vibration decreases for the annealing carried out at 200°C and disappears after the 400°C annealing indicating the evolution of nitrogen compounds probably in the form of nitrogen oxides. This band is also present with a small intensity in the as-prepared and 200°C annealed samples of set B. The explanation for the appearing of this band in set B, it is that small amounts of nitric acid were added to catalyze the hydrolysis/condensation reaction; and some of the copper species reacted to produce copper nitrate species that are, later on, decomposed by the annealing. We can observe from figure 1 that for temperatures higher than 200°C the Si-[OH] band start to increase their relative intensity and broadness, accompanied by the diminishment of the nitrate band, given as consequence an evident modification of the left side of the main (S) band. It is well known that the OH contents decrease, in undoped samples, when a densification induced by temperature is carried out [17]; hence, a noticeable reduction of the band at 950 cm<sup>-1</sup> is observed under these conditions. However, in our A samples we observe the opposite. For figure 2 we observe that this band at 980 cm<sup>-1</sup> is overlapped to the 1078 cm<sup>-1</sup> band even for the as-prepared sample (R-T). If we compare this band for the as prepared samples in both figures, we see that, in the first case (figure 1) the Si-(OH) band corresponding to the Si-O stretching band are no overlapped while in figure 2 the overlapping is very

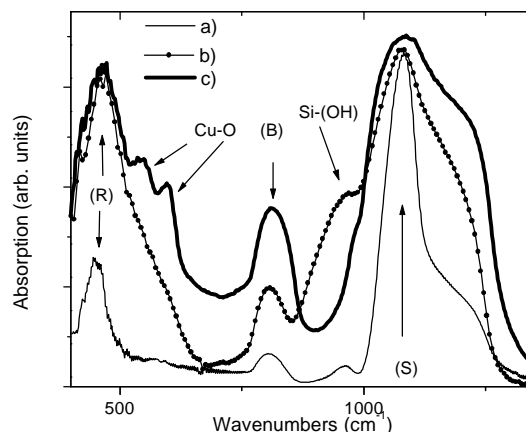


Figure 3 IR absorption spectra in the range of 400 to 1350 cm<sup>-1</sup> for SiO<sub>2</sub> xerogel samples: a) non-doped annealed at 600°C, b) cooper doped annealed at 600°C and c) cooper doped annealed at 800°C

evident. We will discuss in detail this fact in the discussion section.

Figure 3 shows the IR spectra in the 400-1350 cm<sup>-1</sup> for SiO<sub>2</sub> xerogel samples: a) undoped annealed at 600°C, b) copper doped annealed at 600, and c) copper doped annealed at 800°C: the annealing time was 15 minutes. As we mentioned before, the OH contents decreases in undoped xerogel samples when a densification induced by temperature is carried out. From this figure we can see that this is true for the undoped sample, however, for the doped samples we can see how this band overlap the main (S) stretching band at 600°C. For the 800°C sample, the Si-[OH] suffer a noticeable reduction accompanied by a better definition of the Cu-O bands at 530-560 cm<sup>-1</sup>.

Figure 4 shows the X-Ray pattern of the set of samples A annealed at 200°C, 400°C and 600°C. For the 200°C sample, the pattern corresponding to the copper nitrate is still present as the partially hydrolyzed phase

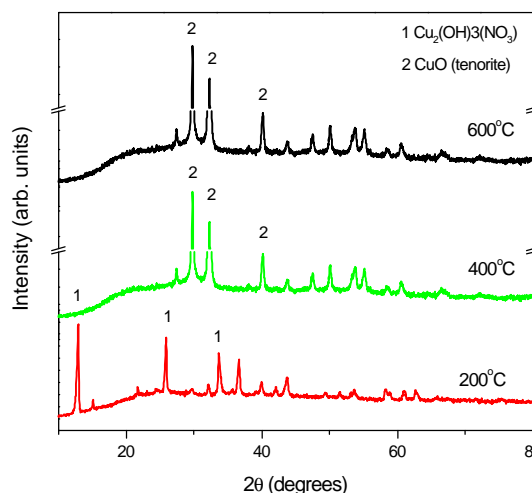


Figure 4 X-Ray pattern samples A annealed at 200°C, 400°C and 600°C

Cu<sub>2</sub>(OH)•3(NO<sub>3</sub>). Considering that the amount of the copper nitrate added to the water is below the limit of solubility and that precautions were taken to totally dissolve it, two situations could occur during the heat treatment of the gel which could explain the later fact: the precipitation of the compounds or the precipitation of separated ions, forming the compounds during the annealing. For the 400°C and 600°C samples we can see the X-ray pattern corresponding to the CuO phase [18].

From these results we can say that for this set of samples there is no evidence of the presence of the Cu<sub>2</sub>O species.

Figure 5 shows the x-ray results of the set of samples B, For the as prepared sample it is possible to see a x-ray pattern with a lot of small peaks corresponding mainly to copper species such as: metallic copper (particles), copper nitrate partially hydrolyzed and cuprite (Cu<sub>2</sub>O). For the sample B annealed at 200°C the peaks corresponding to metallic copper and copper nitrate partially hydrolyzed diminish noticeably and the Cu<sub>2</sub>O peaks are predominant. For the 400°C sample we can observe peaks corresponding to Cu<sub>2</sub>O and CuO with almost the same intensity. Finally, for the 600°C sample the peaks corresponding to the CuO are the predominant features with a very small contribution of the Cu<sub>2</sub>O species.

### 3. Discussion

From our IR and X-Ray results we can conclude that for the samples of set A, there is formation of the copper clusters mainly in form a tenorite, the evolution of the copper species goes from copper nitrate to CuO species. For the copper particles doped samples (set B), the evolution goes from Cu<sup>0</sup> to Cu<sub>2</sub>O, through a intermediate phase Cu<sub>2</sub>(OH)•3(NO<sub>3</sub>) when nitric acid is used, and finally to CuO. It has been reported that the metal-support interaction is carried out by hydrogen; that is the metal or strictly speaking metal oxide particles interact via OH groups. This fact can be corroborated by our IR results, it is well known that the band at 900-980 cm<sup>-1</sup> attributed to the

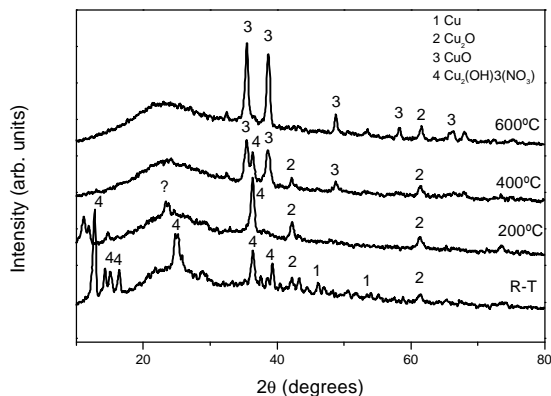


Figure 5 X-Ray pattern of samples B without annealed (R-T) and annealed at 200°C, 400°C and 600°C

Si-OH groups almost disappears in pure silica sol-gels annealed at 600°C. In our samples, this band, is still present for these annealing temperatures, even more the intensity and broadness of this band suffer a noticeable increment with the temperature increment. At 800°C this band almost disappears, indicating the desorption of the hydrogen atoms.

As we have mentioned before, for the as-prepared case in both set of samples, A and B, the IR results show just slight differences. For the A samples the 980 and 1078 cm<sup>-1</sup> bands are well separated one of the other, whereas in the B samples the overlapping of these bands is evident. By using our model we can say that for the as-prepared sample of set A, at this temperatures the copper is mainly incorporated into the SiO<sub>2</sub> matrix as copper nitrate (see fig 1 and 4), there are not copper oxide particles or their concentration is too low. After the copper nitrate decomposition is carried out, the copper oxide (CuO) particles are formed and they interact with the SiO<sub>2</sub> matrix via OH groups. For the B set of samples the overlapping of the Si-(OH) and Si-O stretching band is evident even for the as prepared sample. For this case the copper was incorporated in form of particles or aggregates of these particles, after the incorporation, the copper particles are oxidized to form Cu<sub>2</sub>O and CuO species according to the heat treatment; see fig 5. We can think that in both cases there is a correlation between the existence of metal oxide particles embedded into the SiO<sub>2</sub> matrix and the overlapping of the silanols and Si-O stretching band. As we propose, this overlapping might be associated to the interaction between the guest particles and the matrix host. We have done in previous work a detailed deconvolution of the Si-(OH) band to determining different species of silanols [19].

Using the figure 6 we can illustrate how the metal-glass interact via a hydrogen atoms located at the interface

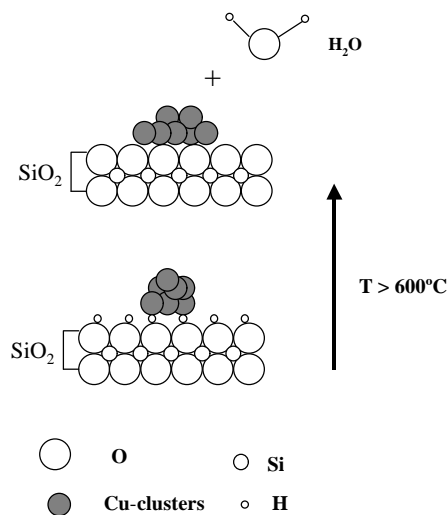


Figure 6 Schematic representation of the metal-glass interaction via an hydrogen atoms located at the interface between the metal particles and the support

between the metal oxide particles and the support. Heat treatments higher than 600°C leads to desorption of the hydrogen and brings the metal based species at direct contact with the oxygen atoms of the support network, for higher temperatures the support material can also chemically interact with the oxide network yielding to the formation of stable compounds like silicate.

#### 4. Conclusions

We have studied clusters of copper based particles. The exact composition of clusters depends on annealing temperature. By heat treatment and chosen the appropriate copper source, we can produce particles of metallic Cu, cuprous and cupric oxide. These metallic clusters composite have an excellent stability and reproducibility. By using IR absorption we are able to study the interaction of the metal based species and the oxide support.

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