



## Copper-Silica Sol-Gel Catalysts: Structural Changes of Cu Species upon Thermal Treatment

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**Abstract.** In this work the encapsulation of copper species in sol-gel silica catalysts thermally treated up to 1100°C was studied. XRD, TPR, BET data showed the occurrence of a vitrification/densification process upon treatment at temperatures higher than 900°C leading to the partial or complete encapsulation of the copper species by the silica matrix. As result of this process the copper catalyst particles become unavailable for the reaction with gas phase molecules and are not active for reactions such as carbon monoxide oxidation.

**Keywords:** copper-silica catalyst, thermal treatment, encapsulation, TPR

### 1. Introduction

Copper dispersed in microporous matrices, e.g. sol-gel silica [1–8] and zeolites, have drawn much attention recently due to its potential catalytic application in environmental processes such as NO<sub>x</sub> reduction [9–11] and hydrocarbon combustion [12–14]. On the other hand, the effect of temperature on these materials has not yet been investigated thoroughly, which is specially important under the high temperatures produced by the exothermic processes during combustion reactions. This work describes the encapsulation of copper species by the silica matrix upon thermal treatment and the effect of this process on the catalytic activity for carbon monoxide oxidation.

### 2. Experimental

Composites were prepared from TEOS (tetraethoxysilane) and, ethanol/water/HCl and HF and CuSO<sub>4</sub> (5% w/w) as described elsewhere [15] and the samples

dried at 110°C for 24 hours, and thermally treated at 500, 900 and 1100°C for 2 hours in air. The samples were analyzed by X-ray diffraction [15] (XRD), BET nitrogen adsorption/desorption (Autosorb instrument Quantachrome Nova 1200). For temperature programmed reduction (TPR) experiments 20 mg samples in a quartz tube under H<sub>2</sub> (8%)/N<sub>2</sub> flow were heated at 10°C·min<sup>-1</sup> up to 700°C and the H<sub>2</sub> consumption monitored by a thermal conductivity detector. The carbon monoxide oxidation was carried out with 15 mg of catalyst with flows of 10 mL·min<sup>-1</sup> CO and 50 mL·min<sup>-1</sup> synthetic air controlled by mass flow controllers. Carbon monoxide consumption was monitored by gas chromatography equipped with FID and TCD detectors (Shimadzu 17A). To produce the copper metal catalysts the materials were reduced in H<sub>2</sub> flow at 500°C for 2 h and characterized by XRD.

### 3. Results

The complete textural characterization of these samples using nitrogen adsorption, mercury porosimetry and positron annihilation techniques has been

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reported in a previous work [15]. The results showed the highest surface area for the materials treated at 110 (Cu110) and 500°C (Cu500), with 254 and 351  $\text{m}^2\cdot\text{g}^{-1}$ , with a significant contribution of micropores. For higher treatment temperatures, 900 (Cu900) and 1100°C (Cu1100), the surface area strongly decreases to 163 and 9  $\text{m}^2\cdot\text{g}^{-1}$ , respectively. This decrease in surface area is accompanied by a density increase from 0.72 to 1.0  $\text{g}\cdot\text{cm}^{-3}$ , which clearly show the occurrence of a densification process of the silica matrix.

### 3.1. XRD Studies

Detailed structural studies of the samples by XRD and EXAFS have been published elsewhere [13, 16]. The XRD patterns [13] for sample Cu110 showed the presence of the  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  phase. After treatment at 500°C the intensity of these diffraction peaks decreased strongly. This is probably related to the thermal decomposition of copper sulfate, which occurred in the temperature range 250–600°C to produce CuO. Upon treatment at 900°C, diffraction peaks characteristic of the phase copper oxide, CuO, were observed. At this temperature the sulfate decomposition was completed and the sintering of the matrix and crystallization of CuO particles took place. After heating the sample at 1100°C both copper oxides, CuO and  $\text{Cu}_2\text{O}$  were observed by powder XRD. These results were corroborated by EXAFS analyses [17].

### 3.2. Temperature Programmed Reduction (TPR) Studies

Figure 1 shows the TPR profiles for the samples treated at different temperatures with their respective  $\text{H}_2$  consumption. In these TPR experiments copper species are reduced to  $\text{Cu}^0$  by  $\text{H}_2$ . The reduction temperature of the copper species will depend mainly on their chemical nature, crystalline phase and also on their location within the matrix [18, 19]. Both  $\text{Cu}^{+2}$  and  $\text{Cu}^{+1}$  are reduced directly in a single step to form  $\text{Cu}^0$  according to the reactions  $\text{Cu}^{+2} \rightarrow \text{Cu}^0$  and  $\text{Cu}^{+1} \rightarrow \text{Cu}^0$  [19].

Sample Cu110 showed three peaks likely related to the reduction of the phases  $\text{CuSO}_4$  (the large peak at 324°C), the main crystalline phase detected by XRD, and two other minor peaks centered at 282 and 244°C probably related to small amounts of copper oxides dispersed on the silica matrix. As the sample was thermally treated at 500°C (sample Cu500) the TPR peak assigned to  $\text{CuSO}_4$  strongly decreased and the other peaks assigned to copper oxide species increased. This result agrees with XRD data, which suggested the thermal decomposition of the copper sulfate to the oxide upon treatment of the sample at 500°C. When the sample was treated at 900 and 1100°C, TPR profiles showed peaks likely related to the reduction of copper oxides (the phases detected by XRD), which are, however, slightly shifted to higher temperatures. This effect is not clear but it might be related to morphologic changes in the silica matrix.

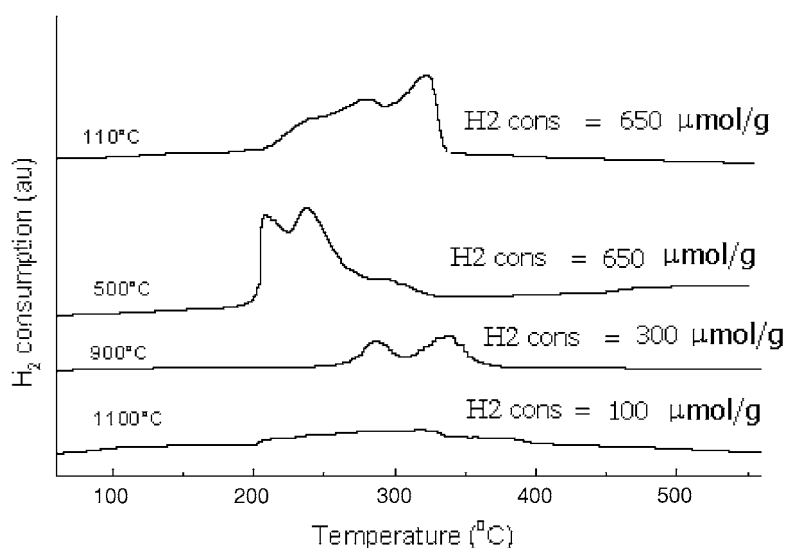


Figure 1. TPR profiles and  $\text{H}_2$  consumption for the samples Cu110, Cu500, Cu900 and Cu1100.

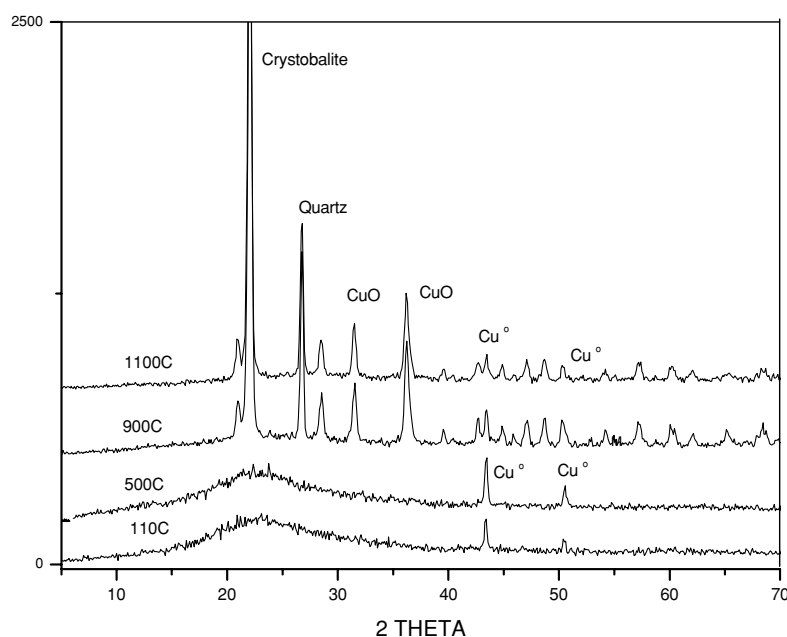


Figure 2. XRD patterns of the samples Cu110, Cu500, Cu900 and Cu1100 reduced with  $H_2$  at  $500^\circ C$ .

The most important feature of these TPR profiles is the hydrogen consumption (the TPR peak area, Fig. 1), which decreases as the treatment temperature increases. For example, sample Cu1100 has only 15% ( $100 \mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}$ ) of the amount of copper species available for reduction, compared to samples Cu110 and Cu500 ( $650 \mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}$ ).

These results could be related to the reduction of copper by the organic compounds present in the silica matrix during the heating treatment. However, no  $\text{Cu}^0$  was observed in either XRD or EXAFS<sup>24,29</sup> measurements after thermal treatment. Moreover, all thermal treatments were carried out in air and a reduced copper form such as  $\text{Cu}^0$  would be unlikely.

### 3.3. $\text{Cu}^0/\text{SiO}_2$ Composites

To produce composites of  $\text{Cu}^0/\text{SiO}_2$  the samples Cu110, Cu500, Cu900 and Cu1100, were reduced with  $H_2$  at  $500^\circ C$  for 2 h. Powder XRD patterns obtained for the reduced samples are shown in Fig. 2. It can be observed that copper in the samples Cu110 and Cu500 was completely reduced to  $\text{Cu}^0$  with particle size of 39 and 34 nm, respectively, as estimated by Scherrer's equation. On the other hand, the XRD analyses of the samples Cu900 and Cu1100 revealed the presence of mainly CuO with small amounts of  $\text{Cu}^0$  (particle size 34 and 79 nm, respectively), showing that copper species

in these samples could not be completely reduced even upon treatment with hydrogen at  $500^\circ C$ .

### 3.4. Catalytic Studies

The copper-silica samples have been tested as catalyst for carbon monoxide oxidation using the catalysts after thermal treatment ( $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ ).

The catalytic activity has been measured in steady state at different temperatures in the range  $150$ – $500^\circ C$ . Figure 3 shows the CO conversions obtained at  $350$  and  $500^\circ C$ .

It can be observed that the catalysts Cu110 and Cu500 show relatively high activity for CO oxidation whereas a strong decrease in activity occurs for the samples Cu900 and Cu1100.

## 4. Discussion

To explain the TPR and the catalytic results the following model, represented schematically in Fig. 4, can be proposed:

The thermal treatment of the copper silica composites at temperatures higher than  $900^\circ C$  causes a significant densification process leading to the encapsulation of copper species. The encapsulated species are not available for the reaction with gas phase molecules,

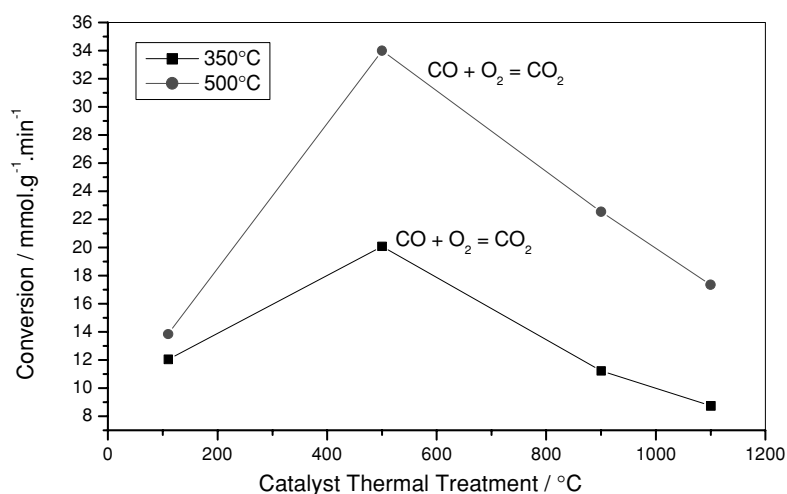


Figure 3. CO conversions obtained at 350 and 500°C in the presence of the catalyst treated at 110, 500, 900 and 1100°C (the catalyst Cu110 was pretreated at 350°C in air or H<sub>2</sub>).

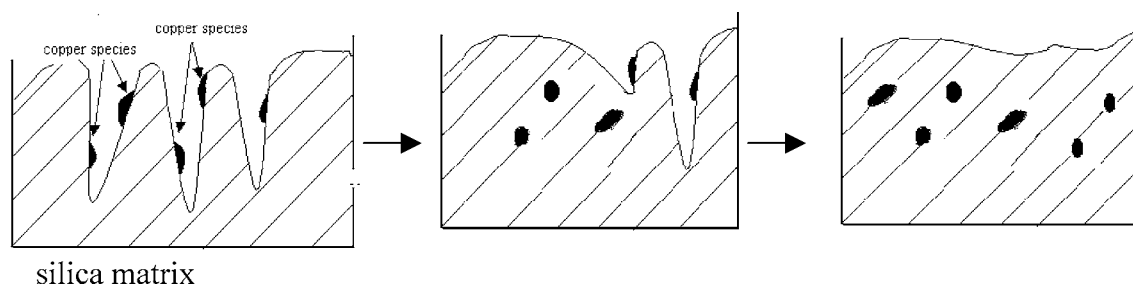


Figure 4. Schematic representation of the encapsulation of copper species in the silica matrix.

what would explain the non reducibility of copper species by H<sub>2</sub> and the lower catalytic activity observed for the samples Cu900 and Cu1100 for the CO oxidation.

## 5. Conclusion

The thermal treatment of sol-gel composite is essential for the preparation of active catalysts. The composites treated at 500°C presented more activity than the other due to their greater surface area that increase the catalytic activity. This activity declined drastically for samples treated at 900°C due to the densification of the SiO<sub>2</sub> matrix, which provoked a decrease in surface area and the entrapment of copper species.

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