

Effect of Concentration and Thermal Treatment on the Properties of Sol-Gel Derived CuO/SiO₂ Nanostructure

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ABSTRACT: Various concentrations of copper are embedded into silica matrix to xerogel form using copper source - $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The xerogel samples are prepared by hydrolysis and condensation of tetraethyl orthosilicate (TEOS) by the sol-gel method and with determination of new molar ratio of components $\text{H}_2\text{O}/\text{TEOS}$ to be 6.2. In this investigation, the necessary amount of trihydrated copper nitrate is added to the solution in such a manner that the concentration of the copper oxide in final solution reach to 1, 2 and 5 wt% (samples A, B and C respectively). After ambient drying, the gel samples are heated from 60 to 1000 °C at a slow heating rate (50 °C/h). The absorption and transmittance spectrum of various concentrations of copper are studied by Uv-vis spectrophotometer. Thermal treatment effects are characterized by FTIR, TGA, TEM, SEM, XRD, BET and TPR methods at different temperatures.

KEY WORDS: Copper oxide, Nanocomposite, Concentration, Thermal treatment, Silica.

INTRODUCTION

Organic and inorganic materials molecular chemistry has had great progress during the last few decades. Apart from polymer materials, most ceramic and glass materials are prepared by solid state reactions. The main exception, when the synthetic methods are based on a molecular

chemistry approach, is the preparation of oxides by sol-gel method [1]. The sol-gel method have been well studied and developed in materials science since they are well suited for preparing and designing devices with very specific properties [2]. The sol-gel processes may be

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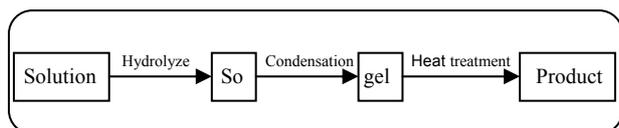


Fig. 1: Total pattern of sol gel process.

divided into two classes depending on the nature of the precursors; inorganic precursors (chlorides, nitrate, sulfides, and etc.) and alkoxide precursors. The route that involves the use of alkoxide precursors appears as the more versatile one [3].

Fig. 1 exhibits total pattern of sol gel process. Sol-gel method is a relatively new technique for preparation of glasses to get high purity and homogeneity at low temperatures processing [4]. Introducing transition metal into hydrolysable precursors through sol-gel methods permits the formation of numerous novel materials that exhibit important optical and/or catalytic properties [5, 6]. Copper or copper oxides in oxide matrixes have attracted sustained interest due to their unusual properties [7]. *Mohanani & Brock* [8] have studied copper oxide silica aerogel composites by varying pH values, copper precursor salts, and treatment temperatures. They found that based-catalyzed gels underwent a gradual change from bonded Cu^{+2} to segregated CuO at different heating conditions. *Parler et al.* [9] observed silicon-oxygen-metal bond formation during both synthesis and drying stages at low temperatures with relative high copper concentrations. *Dutta et al.* have studied sol-gel nanocomposites containing copper and their gas sensing properties [10]. Also, the selective catalytic reductions of oxide-supported copper have reported in ref [11]. Some properties such as bacterial inhibitory capacity depend highly on the copper ion complex state at lower concentrations [12]. In recent study, host matrices have been extensively embedded with copper oxide that was produced with different copper concentrations (between 1-5 wt%) and examined during gelation and drying. The characterization of the xerogels are examined by Uv-vis, FTIR, TGA, TEM, SEM, XRD, BET and TPR methods at different temperatures [13].

EXPERIMENTAL SECTION

Materials

In this investigation the raw materials consist of tetraethyl orthosilicate (TEOS) (Fluka, 98%),

ethanol absolute (EtOH) (Merck), copper nitrate trihydrated (Merck), as initial solution and HNO_3 (Merck, 65%), CH_3COOH (Merck, 99-100%) as catalysts, were used with the mentioned specification.

Sample preparation

Three samples of CuO/SiO_2 nanocomposite to xerogel form were prepared by the sol-gel method and another one was prepared as a blank sample using TEOS hydrolyzed with HNO_3 and CH_3COOH , ethanol and DI water with new total molar ratio of $\text{TEOS}:\text{EtOH}:\text{H}_2\text{O} = 1:1.3:6.2$ [8]. The necessary amount of trihydrated copper nitrate was added to solution such that the concentrations of copper oxide in the final product reach to 1, 2 and 5 wt% (samples A, B and C, respectively). Then the solutions were mixed by magnetic stirrer for 1.5 h, to make them more homogeneous. The solution acidity (pH) was measured by pH-meter which was reported 2.4. The samples are kept in a close container at 25-30 °C temperature. The soft gel was prepared till dark-blue color appeared along 84 hrs (3.5 days) via gelation treatment. Then the gel samples were dried in an oven at 60-100°C temperature in air atmosphere for 1h, to complete the gelation process. The gel samples were annealed by electrical furnace in the range of 100-1000 °C at 50 °C/h for 2 h, to form the condense nanocomposites [14]. The blank solution was prepared without addition of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with the mention methods.

Characterization

Uv-vis spectrum was determined by BEKMAN (DU-600) UV Spectrophotometer.

Fourier transmission infrared spectroscopy (FTIR) spectrum, was carried out by a Gensis system, model ATI, using 0.05 g of powder sample with 0.3 g of KBr.

TPR (Temperature-Programmed Reduction) was used to investigate the availability of copper species for the reaction with gas-phase molecules. These results can be correlated with catalytic activity such as carbon monoxide oxidation. The sol-gel samples were used for the TPR directly after the thermal treatment with no pre-activation. For TPR experiments, 20 mg samples in a quartz tube under H_2 (8%)/ N_2 flow were heated at 10°C min^{-1} up to 700°C and the H_2 consumption monitored by a Thermal Conductivity Detector (TCD).

Thermal Gravimetric Analysis (TGA) was obtained

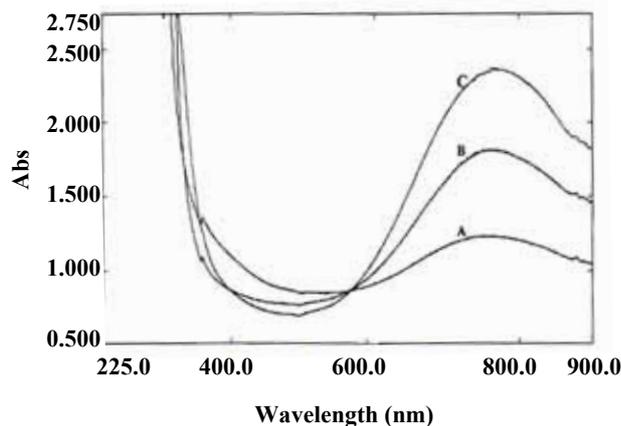


Fig. 2: Absorption spectrum of samples (A, B and C) heated at 200 °C.

by Rheometric Scientific Instrument, model STA 1500.

The acidity of solution (pH) was measured by Omega pH-meter, model 744.

The condensation and annealing of the samples was done in an Oxaiton heat furnace with high thermal capacity (1500 °C).

A transmission electron microscope (TEM) Em208S series, made by Phillips Company, operating at 100 kV was used for this investigation. The dry samples were ground suspended in dry cyclohexane and sonicated for 30 minutes. Then the solutions were allowed to settle and a droplet of the resulting supernatant was placed on a holey carbon film and dried.

A scanning electron microscope (SEM) XL-30 series, made by Phillips Company, was used. The samples were powdered and coated with gold, before the examination by SEM.

The X-ray diffraction (XRD) patterns were performed in a Philips diffractometer model PW1800 using copper anodic tube with wavelength of 1.54 Å.

The porosities of the samples were analyzed by nitrogen adsorption/desorption measurements fitted to a BET isotherm using an Autosorb instrument (Quanta-chrome, Nova 1200). The samples were pre-treated for 3 hours under vacuum at 100 °C (for the sample dried at 100 °C) and at 200 °C (for samples treated at 400, 800 and 1000 °C). Gaseous nitrogen was used with a 5 hours adsorption/desorption cycle.

RESULTS AND DISCUSSION

Physico-chemical characteristics

Fig. 2 presents the absorption spectrum of samples A,

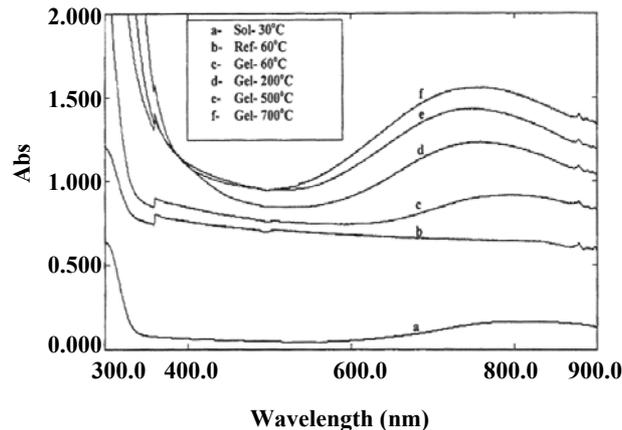


Fig. 3: Absorption spectrum of sample A heated at different temperatures.

B and C heated at 200 °C of temperature. From this spectrum we observe all the doped gel samples present an absorption band in around 780 nm wavelength, which explains the presence of Cu^{+2} ions in the gel matrix [15]. This absorption intensity increases for higher concentration of copper ions in volume unit. Fig. 3 shows absorption spectrum of sample A (1wt%) at different temperatures of 30(sol), 60(Ref), 200, 500 and 700 °C. This figure presents that the broad absorption band shifts toward shorter wavelength due to the raising of temperature, as well. It is well known that diluted copper(II) ions in silica matrix exhibit the broad optical absorption band in around 780 nm related to electronic transfers due to d levels splitting of copper(II) ions in a ligand field. This broad absorption band is in NIR (Near Infra Red) region for the samples heated at 60-700 °C temperatures. The band wavelength shifts from 750-790 nm region and the broad band shifts from 700-900 nm to 600-800 nm region, i.e., edge of red absorption energy decreases from 700 to 600 nm. There are $d-d$ electronic absorption transmissions in each diagrams, and the broad band in around 780 nm related to electronic transmission of d orbital [16]. The absorption edge shift has been exhibited as charge transfer agent between copper ions and ligands of matrix. It is suggested that the broad absorption in around 780 nm in xerogel is attributed to the presence of copper (II) ions in internal position of silica matrix [16]. The shift of broad absorption toward lower wavelength indicates that, by raising of temperature, water molecules are removed and the shrinkage of ligand field increases.

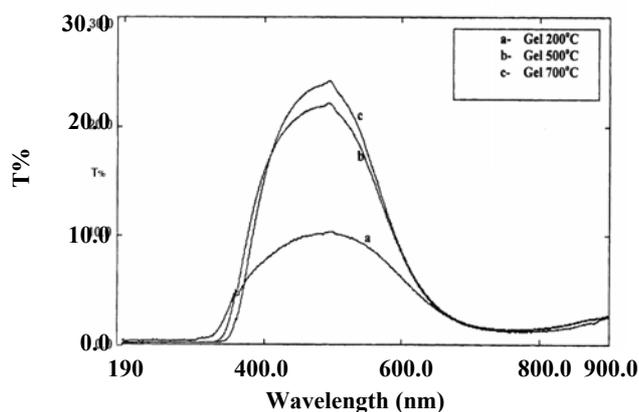


Fig. 4: Transmittance spectrum of sample (B) heated at 200, 500 and 700 °C.

Impurity of water in oxides appears in the form of hydroxy groups form that produce absorption band in NIR region [15]. Sometimes it is observed that an absorption band in violet region (400 nm) exhibits CuO colloidal particles in the matrix [15]. But it is surprising that no absorption band is seen in this range. This is due to the low concentration of copper ions and low acidity of the samples. Fig. 4 presents transmittance spectrum of the sample B (2wt%) that is heated in different temperatures (200, 500 and 700°C). The blue color of gel samples is interpreted by transmittance spectrum that indicates maximum transmittance in 400-600 nm range. Because of high purity and low amount of water, these nanocomposites show high transmittance. These observations indicate that the samples present filtering effect in the 400-600 nm range [17].

The bonding and molecular structure property of CuO/SiO₂ nanocomposite was done in bonding vibrational mode by FTIR spectrum. Fig.5 presents the FTIR absorbance spectrum in the range of 500-4000 cm⁻¹ for SiO₂:CuO in the powdered sample. Fig.5 is the FTIR spectrum of copper ions (5 wt%) doped in silica matrix heated at 500°C and 900°C. In this figure, it can be seen that the hydroxyl groups are removed at 900°C, although molecular water can be taken away at about 200°C. However, hydroxyl groups can be removed in temperature range of 800-1000°C. The absorption band in the range of 1450 cm⁻¹ related to reduction of nitrate groups in the solution with increasing temperature, presents complete decomposition of these groups at 900°C.

The main bond of the SiO₂ FTIR spectrum is due to

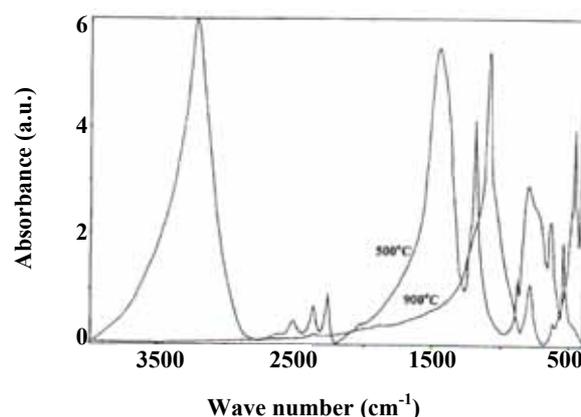


Fig. 5: FTIR spectrum of CuO/SiO₂ (C) at 500 and 900 °C.

the asymmetric stretching mode at region 1150-1250 cm⁻¹, whereas, this sharp band shifts to lower wave number at 900°C [18]. The absorption band in 900-1000 cm⁻¹ is assigned to Si-OH groups, due to often disappearing of these groups in heated pure silica. FTIR spectrum of CuO/SiO₂ xerogel sample at 900°C presents that the absorption bands in 950 and 1200 cm⁻¹ are separated from each other. But, the FTIR spectrum at 500°C presents overlapping of Si-OH and Si-O bands.

Fig. 6 shows the TGA analysis of Cu(NO₃)₂/SiO₂ at 30-300°C temperatures. There is a weight loss about 1mg at 30-100°C, due to the evaporation of residual alcohol and water at 100°C. In the temperature range of 100-200°C, the weight loss is constant and no significant weight loss was observed at these temperatures, but at the range of 200-300°C, we see a small weight decrease, probably related to the thermal decomposition of surface hydroxyl and ethoxyl groups.

Structural analysis

The microstructure of the xerogel was examined by TEM. Powder samples with 5wt% copper after ambient drying and thermal treatment at 400°C in air for 1h, were objected to TEM using bright field, and the resulted image is shown in Fig. 7. No crystalline species were detected without thermal treatment, and bright field image shows a typical amorphous xerogel. After heating at 400°C, copper species start to segregate. This figure confirms the formation of average size of about 50 nm. Fig.8 presents the X-ray pattern of the CuO/SiO₂ sample sets annealed at 200, 400 and 600°C. For the sample

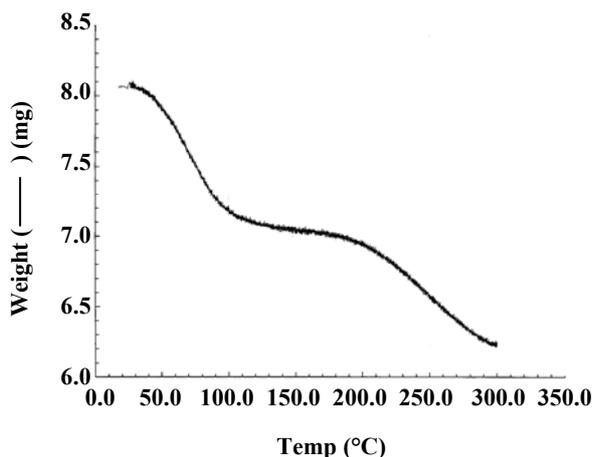


Fig. 6: Thermal analysis of $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ (A) nanocomposite.

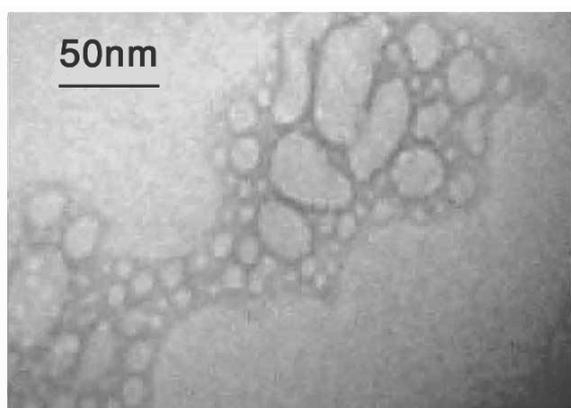


Fig. 7: TEM micrograph of CuO/SiO_2 nanocomposite (A) at 400°C.

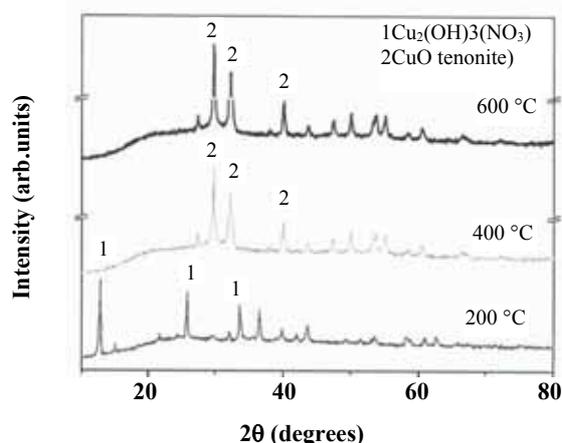


Fig. 8: X-ray pattern CuO/SiO_2 sample (C) annealed at 200, 400 and 600°C.

annealed at 200°C, the pattern corresponding to the copper nitrate is still presented as the partially hydrolyzed phase $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$.

Although the amount of the added copper nitrate is below the limit of solubility and all precautions were taken to dissolve it, two states could occur during the thermal treatment of the gel, which explain the later fact that the precipitation of the compounds or separated ions lead to formation of the compounds during the annealing. For the samples annealed at 400 and 600°C (C), it can be seen the X-ray pattern corresponding to the CuO phase in Tenonite structure [17]. From these results it can be said that there is no evidence of the presence of Cu_2O species in these samples, but for the samples A and B, X-ray diffraction patterns are not clear at these temperatures. Because, we think the amounts of copper nitrate are very low.

The backscattered electron images of the samples present well-defined regions with 5 wt% copper by SEM at 100, 400, 800 and 1000°C exhibited in Figs.9 and 10. At 100°C, it can be seen that the copper nitrate particles are embedded in the silica matrix, but with increasing temperature at 400-800°C, the copper nitrate particles are decomposed and converted to copper oxide particles that doped into the silica matrix. By thermal treatment at 1000°C, the copper oxide particles are decomposed and form an oxide network containing metal oxide clusters like Cu-O-Cu that are connected to silica support. This process completely depends on the thermal treatment effects and copper source. These metallic nano clusters have a structure with excellent stability and reproducibility [16].

It is reported that interaction of support and metal is performed by hydrogen atom i.e. metal or metal oxide interacts with hydroxyl groups. We can say that copper ions are doped into silica matrix to form copper nitrate and there are no more copper oxide particles. But with raising temperature and decomposition of copper nitrate, the copper oxide particles are formed and interact with silica matrix by OH. It can also be concluded that there is a relation between existence of copper oxide in silica matrix, and overlapping of silanol groups and Si-O bands in infrared spectrum at 500°C. This overlapping leads to interaction between guest particles and host support.

Fig.11 illustrates the thermal treatment effects on the metal-glass interaction via hydrogen atom located at the

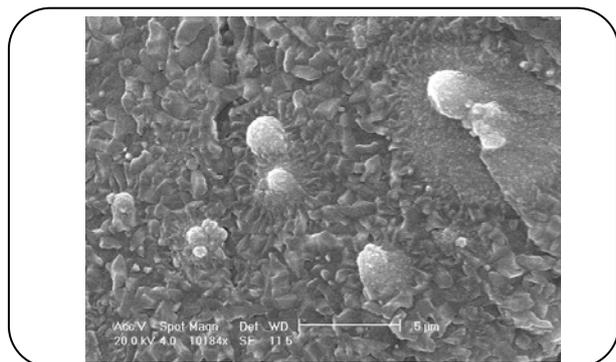


Fig. 9: SEM micrograph of copper nitrate on the silica matrix at 100°C.

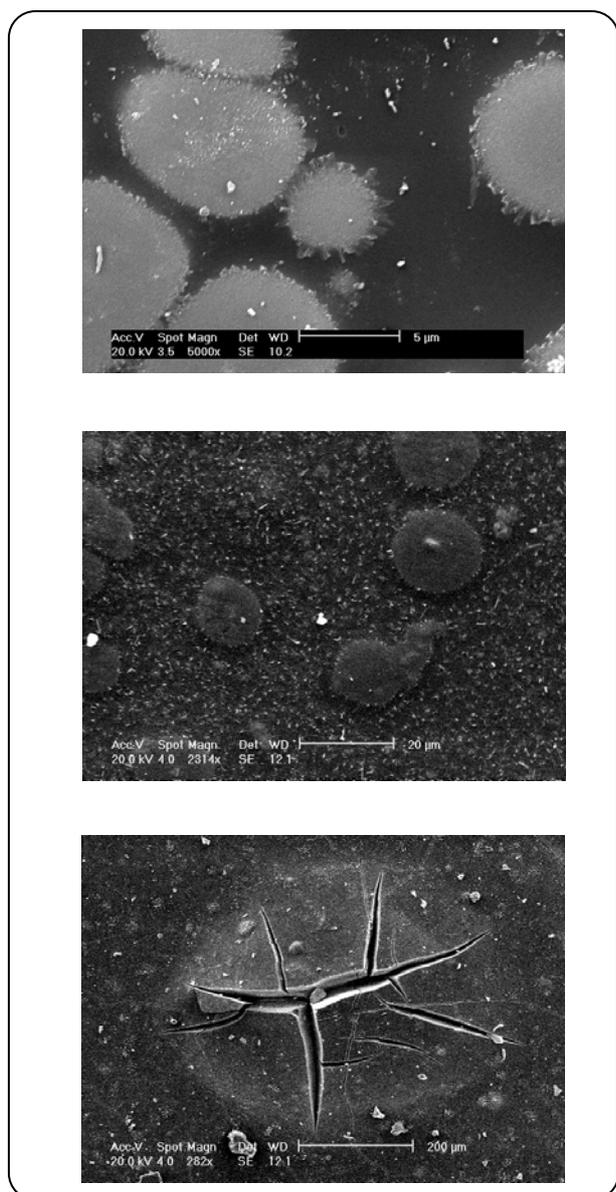


Fig. 10: SEM micrograph of copper oxide in the silica matrix at 400 (a), 800 (b) and 1000°C (c).

interface between the metal oxide particles and the support.

Thermal treatment 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. The effect of the thermal treatment on the textural properties of the sol-gel samples is presented in Table 1. The obtained data shows that the treatment at 400°C produced the largest surface area, pore size radius with the lowest density.

These results indicate the loss of volatile compounds from the porous structure. Once the volatile compounds are eliminated from the network, an increase occurs in the porosity and the gas pore interface. Despite this weight loss, a little shrinkage is observed for the material treated at 400°C, resulting to density decrease. It is interesting for the sample treated at 400°C, to have a surface area increases by 38% (from 254 to 351 m²·g⁻¹), whereas the pore volume shows a much more pronounced increase of 211.7% (from 196 to 611 cm³·g⁻¹). For the sample treated at 800°C, the surface area decreases by 53.5%, whereas the pore volume shows reduction of 76.6%. Also, for the sample treated at 1000°C, a surface area decrement of 95% is observed, whereas the pore volume shows a reduction of 92.3% and porosity decrease of 64.3% (from 14 to 5 Å). Although, this effect is not clear, in authors view it is related to the size and shape of micro, meso and macro-porous, which are modified as the sample is treated at different temperatures. For the higher temperatures (800 and 1000°C) the surface area and porosity strongly decrease due to densification process. The results have presented a significant contribution of micro-porous in the material treated at 100 and 400°C. For higher thermal treatment, the surface area decreases due to the presence of micro and meso-porous, but the contribution of the meso-porous area in the total surface progressively increases [18].

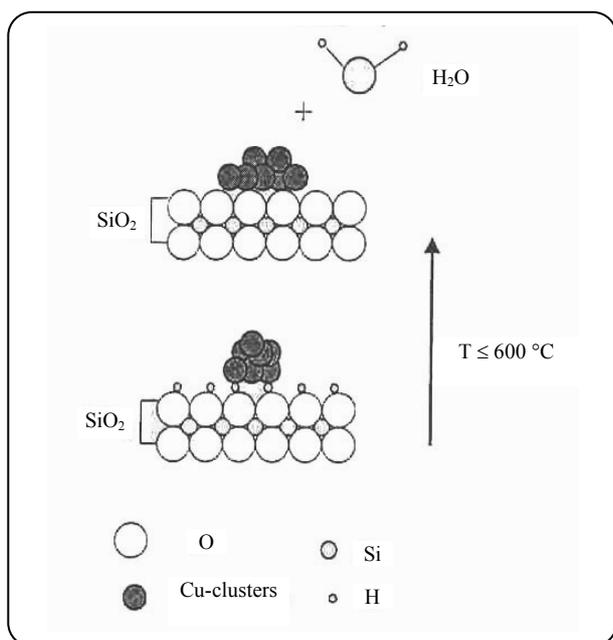
TPR Studies

Thermal Program Reduction experiments (TPR) have shown the reduction of copper species to Cu⁰ by H₂. Both Cu⁺² and Cu⁺¹ are reduced directly in a single step to form Cu⁰ according to the reactions Cu⁺² → Cu⁰ and Cu⁺¹ → Cu⁰. TPR analysis of the samples treated at different temperatures is presented in Fig.12.

The TPR profile of the sample Cu100 shows three hydrogen consumption peaks; a large peak at 325°C (1),

Table 1: Thermal treatment effects on the surface area, porosity and density of CuO-Silica.

Sample	T(°C)	Surface area (m ² g ⁻¹)	Pore radius (Å)	ρ_{pic} (g cm ⁻³)	V_p (cm ³ g ⁻¹)
Cu100	100	254	12	0.72	196
Cu400	400	351	17	0.7	611
Cu800	800	163	14	0.74	143
Cu1000	1000	8	5	0.98	11

**Fig. 11: Schematic representation of the thermal treatment effect of copper-glass interaction via hydrogen atom at 600 °C.**

and two minor ones at 280 (2) and 245 °C (3). For sample Cu400, the TPR profile is shifted at ~25 °C to lower temperatures. The largest peak observed for sample Cu400 at 290 °C (1) was much smaller and the other peaks at 255 (2) and 220 °C (3) increased in intensity. These results indicate that peak (1) is related to the reduction of Cu(NO₃)₂ and the peaks (2) and (3) are due to the reduction of copper oxides. When the sample was treated at 800 °C, TPR profiles were shifted back to higher temperature and peak (1) related to Cu(NO₃)₂ was absent, whereas peaks (2) and (3) related to copper oxides, increased strongly in intensity. At 1000 °C, TPR profiles showed that the peaks (2) and (3) are mixed together and form a broad peak. It can also be observed that the hydrogen consumption decreases as treatment

temperature increases, according to the results indicated in Table 2.

Samples annealed at 800 and 1000 °C only have 46% and 15% of amount of copper species available for reduction, in comparison to the samples annealed at 100 and 400 °C, respectively. These results could be related to the reduction of copper by the organic compounds present in the silica matrix during the heating treatment. Moreover, all thermal treatments were carried out in air and a reduced copper form such as Cu⁰ would be unlikely. To explain the decrease in TPR of H₂ consumption, one can envisage that treatment at temperatures higher than 800 °C, the densification process with sintering and closing of the pores may lead to an entrapment of copper species in the vitreous silica matrix. The entrapped copper species will not be available on the surface for the reaction with H₂ during TPR experiments.

CONCLUSIONS

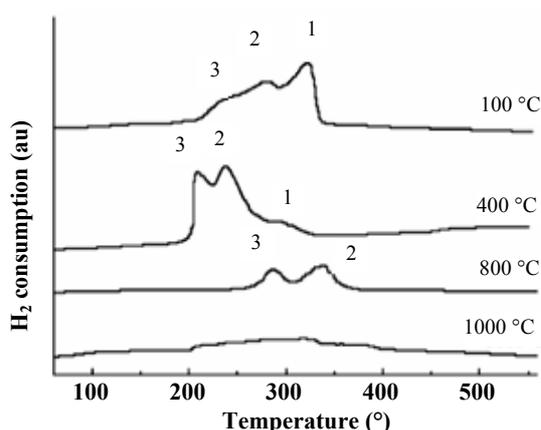
The incorporation of copper ions in the matrix up to 700 °C was confirmed by absorption spectrums. The broad absorption band of Cu²⁺ ions in around 780 nm is related to the ligand field splitting of d levels. The partial removal of hydroxyl groups is confirmed by shifting the broad band to higher energy region. FTIR measurements confirm the removal of hydroxyl groups from the samples at 900 °C temperature. TEM micrograph confirms the formation of colloidal particles of about 50 nm size. The transmittance spectrum of high temperature treated copper doped into silica matrix indicates the broad band with filtering effect.

X-ray results shows that for CuO/SiO₂ samples, there is formation of the copper clusters mainly in the form of a tenorite. The evolution of the copper species goes from copper nitrate to copper oxide species by thermal treatment. It has been reported that the metal-support interaction is carried out by hydrogen that is the metal or metal oxide particles interact via OH groups. This fact can be corroborated by FTIR results. It is well known that the band at 850-990 cm⁻¹ attributed to the Si-OH groups.

The FTIR results show that the copper ions are mainly incorporated into the SiO₂ matrix in copper nitrate form, and there are not copper oxide (CuO) particles, or their concentration is too low. After decomposition of the copper nitrate, the CuO particles are formed and they interact with the SiO₂ matrix via OH groups. The SEM

Table 2: TPR of H₂ consumption for CuO/SiO₂.

Treatment temperature (°C)	H ₂ consumption (mol g ⁻¹)	Relative H ₂ consumption (%)
100°C	650	100
400°C	650	100
800°C	300	46
1000°C	100	15

Fig. 12: The TPR profiles of Cu(NO₃)₂-SiO₂ samples treated at 100, 400, 800 and 1000°C.

images exhibit that the copper nitrate particles are embedded in the silica matrix, but with increasing temperature at 400-800°C, the copper nitrate particles are decomposed and converted to copper oxide particles that doped into the silica matrix. By thermal treatment, at 1000°C, the copper oxide particles are decomposed and form a oxide network containing metal oxide clusters like Cu-O-Cu that are connected to silica support. Thermal Program Reduction experiments (TPR) show the reduction of copper species to Cu⁰ by H₂. Both Cu⁺² and Cu⁺¹ are reduced directly in a single step to the form of Cu⁰ according to the reactions Cu⁺² → Cu⁰ and Cu⁺¹ → Cu⁰. Also, this experiments present relation between H₂ consumption and temperature.

In the author view, there is a correlation between the existence of copper oxide particles embedded into the silica matrix, and the overlapping of the silanol and Si-O stretching bond. This overlapping might be associated to the interaction between the guest particles and the matrix host [19]. According to this study the exact composition of clusters depends on the annealing temperatures and the choice of appropriate copper source.

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