COMPARISION NANOSTRUCTURE BEHAVIOR OF COPPER SPECIES ON THE SILICA MATRIX XEROGELS

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Abstract Incorporation of copper species in a silica matrix is carried out using sol-gel method. Copper ions and copper particles were chemically synthesized and incorporated in the matrix using two different copper sources of $Cu(NO_3)_2.3H_2O$ and copper particles. The particles of copper metallic, cuprous and cupric oxide were prepared and synthesis and characterization of copper species on the silica matrix were compared.

Keywords Synthesis, Charactrization, Sol Gel Process, Copper Species

چکیده دراین گزارش جا سازی گونه های مختلف عنصر مس در بستر سیلیکا با روش سل -ژل انجام شد. با استفاده از نیترات مس ۳ آبه وبا روش شیمیایی تولید ذرات مس ، یون های مس۲ و ذرات فلز مس در بستر سیلیکا قرارگرفته است. در این تحقیق، تهیه و خصلت یابی گونه های مس روی بستر سیلیکا مانند ذرات فلزی مس، و اکسید های مس ۱و۲ را با هم مقایسه شده است.

1. INTRODUCTION

The sol-gel method is a versatile technique for preparation of glass coating and powdered samples that allows the incorporation of metals sand other materials in their matrixes [1, 2]. The incorporations of different elements, post deposition treatments and the interactions of the elements with the host matrix lead to the modifications of the glass structure [1]. The introduction of transition metals in a SiO_2 glass matrix has a strong influence on the optical visible absorption spectrum [3]. Nano and micro size particles of various materials embedded in the glass matrix produce quantum and non linear optical effects when the particles have some critical size [4].

In the sol-gel method, metal ions can be doped into ionic oxide network, and are converted to more stable compounds to other methods [5,6].The sol-gel polymerization of metal alkoxides in presence of inorganic salts lead to the formation of ceramic oxides materials with important micro-structural properties [7]. Several authors have reported the works concerning sol-gel prepared silica samples containing copper [8,9], they have also checked various steps of preparation CuO/SiO_2 by the sol-gel method [10]. To our knowledge, none have compared the preparation and characterization of different copper species by analytical instruments. The main suggestion of this investigation is doping copper species in the silica network by thermal treatment and explore the nanostructure of the support material and the evolution of metallic species in the silica network.

2. EXPERIMENTAL DETAILS

In this investigation, the raw materials contain tetraethyl ortho-silicate (Fluka, 98%) (TEOS), ethanol absolute (Merck) (EtOH), copper nitrate tri-hydrated (Merck), HNO_3 (Merck, 65%), CH_3COOH (Merck, 99-100%) were used. Initially, samples were prepared by sol-gel method as CuO/SiO_2 nano-composite xerogel [10]. The Initial solution for CuO/SiO_2 xerogel was prepared with mixture of TEOS, H_2O, ETOH, $Cu(NO_3)_2$. $3H_2O$, 3M HNO_3, 4M CH_3COOH, with total molar ratios of 1:1.3:6.2 for TEOS: EtOH:H_2O. Subsequently, 0.2 moles of Cu $(NO_3)_2$. $3H_2O$, 5 x 10^{-3} moles of 3 M HNO_3, 4 x 10^{-3} moles of 4 M CH_3COOH were added to 1mole of TEOS for catalyzing the hydrolyzation and condensation reactions. A homogenous solution of all components was obtained after mixing them for 2.5 hours by a magnetic stirrer. The final pH of all the samples was about 2.4. The solution was kept in a close container at 25-30 ^oC. The soft gel was prepared to dark- blue color in 84 hours (3.5 days) by gelation treatment. Then gel samples were dried in an oven at about 100 ^oC in air for 2 hours and the gelation procedure was thus completed. Copper particles were obtained using a water oil microemulsion and using $NaBH_4$ as the reducing agent.

Microemulsions were prepared by dissolving aqueous $CuCl_2$ or $NaBH_4$ solution into a surfactant/hexanol/hexane solution. $CuCl_2$ is dissolved in one solution and $NaBH_4$ in the other one, where, the salt concentrations in the aqueous phases were 0.1 M in $CuCl_2$ and 0.3 M in $NaBH_4$. Preparation of copper particles was carried out by rapidly mixing equal volumes of each water/microemulsion ratio; and pH of $CuCl_2$ solution, the amount of Cu_2O present in the copper particles can very drastically. The copper particles are made at room temperature without removing the oxygen [8]. For the particle-doped xerogels, they were mixed with ethanol directly to the homogenous H_2O/TEOS solution and hence the final solution was obtained. The solution was then stirred for about 15 minutes by a magnetic stirrer. The two solutions were placed in a container at constant temperature bath at 35 ^oC. The samples were labeled set A for the copper nitrate and set B for the particles one. In both sets of samples, soft species were obtained after about 48 hours. The B solutions were heated in an oven in air atmosphere at about 100 ^oC to produce rapidly dried the solution and thus accelerating the gelation process. For subsequent annealing, the samples were introduced in the oven at the desired temperature for 25 minutes in air. These species were ground to form a fine powder.

-The infrared spectra were prepared in a FTIR spectrometer of Gensis system- model ATI, using 0.05 g of powder sample with 0.3 g of KBr.

-TEM micrographs were prepared using a Phillips system- model Em208S at 100 kV. The dry samples were ground and suspended in dry Cyclohexane, and sonicated for 1-2 minutes. Then, the solution was allowed to settle and a droplet of the resulting supernatant was placed on a carbon film and dried.

-The x-ray diffraction (XRD) patterns were Prepared by a Philips instrument using PW1800 Diffractometer and radiation of Copper Anodic Tube λ=1.54A$^{\circ}$.

- Scanning electronic microscopy (SEM) was performed by SEM XLC Philips instrument.

-The acidity of solution (*P*H) was measured by Omega *P*H meter-model 744.

-The condensation of samples was done in a heat furnace (Oxidation model) with high thermal capacity (1500 °C).

3. DISCUSSION AND RESULTS

The bonding and molecular structure of Cu,CuO/SiO_2 nanocomposites were studied using in bonding vibrational mode in the range of 400 to 2200 cm^{-1} by FTIR spectrum. Figures 1 and 2 present the FTIR absorption spectrum for SiO_2: CuO and SiO_2: Cu in powdered sample form. We can see three main regions from 400 to 1300 cm^{-1} and labeled (R), (B) and (S) respectively. Each of the three major features related to transversal optical (TO) absorption bands is shown in figures 1 and 2 which can be characterized in terms of a particular vibration mode of the oxygen atom with respect to the silicon atom that can be linked. Rocking (R) of the oxygen atom about an axis through the two Si atoms characterize the

vibrational behavior of the lowest frequency to bond central at 450-490 cm^{-1}. Bending (B) of the oxygen atom along a line bisecting the axis was formed by the two silicon atoms characterizes the vibrational mode of the middle TO band at 780-810 cm^{-1} [11]. The remaining TO band and its high frequency shoulder are due to an asymmetrical stretch (S) motion in which the oxygen atom moves back and forth along a line parallel to the axis through the two silicon atoms [12].

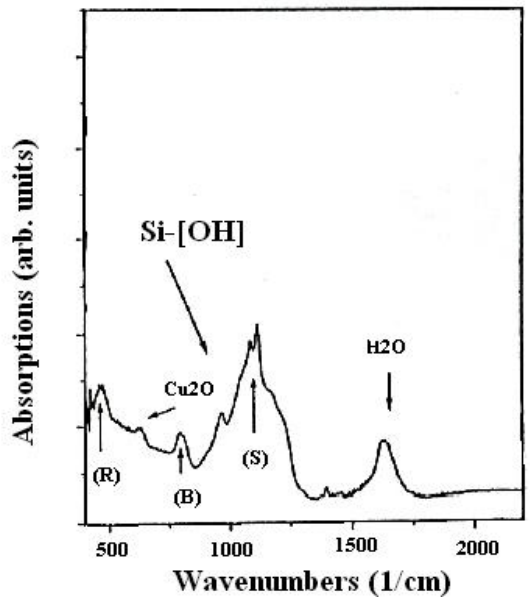

Figure 1. FTIR spectrum of CuO/SiO_2 nanocomposite

The main band of the SiO_2 FTIR spectrum corresponds to the asymmetrical stretching (S) mode at 1100 cm^{-1}. It has been reported that the FTIR spectrum in which a shoulder, in the frequency range of 1150 to 1250 cm^{-1}, has an amplitude comparable or bigger than the main stretching band at 1100 cm^{-1} [13,14]. This has been achieved in vitreous SiO_2 samples prepared by the sol-gel method using specific preparation conditions. Also, from Figures 1 and 2 we can observe a band at 850-990 cm^{-1} assigned to the vibration of the [Si—OH] groups.

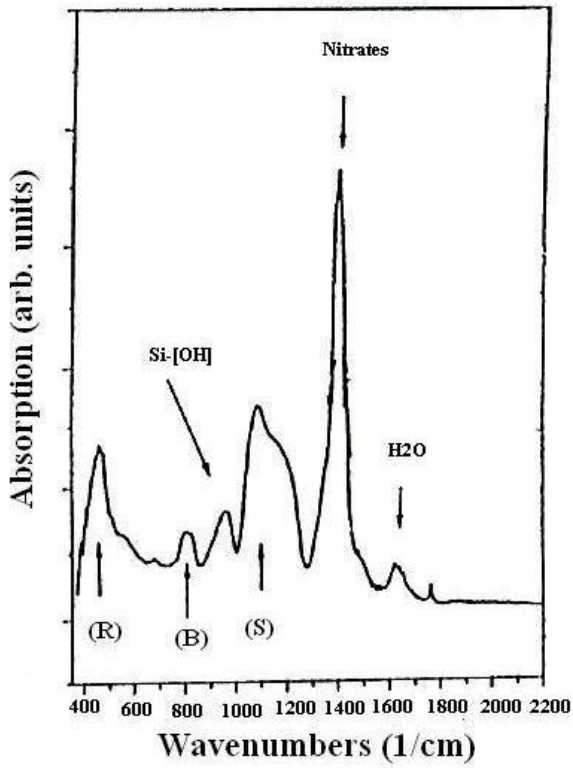

Figure 2. FTIR absorption of Cu/SiO_2 powdered sample

In Figure 1, we have this band and bending band Si—O (B) that observed to separate peak type of stretching frequency Si—O (S) in set A, but in Figure 2, we can see the overlap of Si–OH band and stretching frequency Si—O (S) in ambient temperature in set B [15]. If we compare this bond for the as prepared samples in both figures, we see in Figure 1 that the [Si—OH] band and Si—O (S) stretching band do not have any overlap, while in Figure 2, the overlapping is quite evident. It has been reported that the Cu—O vibration in cupric oxide has IR active modes at 420, 425 and 528 cm^{-1} [13], Figure 1 shows two separate peaks related to (R) and Cu—O, but, Figure 2 confirms overlapping of these two peaks in this range. Therefore, the relative increase in the intensity of the (R) band could be the consequence of overlapping of the (R) band and Cu–O bands. In spectrum of B samples, there is an additional band about 620 cm^{-1} that can be due to vibrational modes of Cu–O in Cu_2O phase [14].

There are two additional bands at about 1450 and 1650 cm^{-1} related to the nitrate groups and free molecular water vibrations respectively [16]. In set B, the peak of nitrate groups is very sharp, but, in set A this peak is very small, because small amounts of nitric acid has been added to catalyze the hydrolysis/condensation reactions. The microstructure of the xerogel was examined by transmission electron microscopy (TEM). Powders with copper particles and copper ions after ambient drying and thermal treatment at 400°C in air for 1hour were imaged on TEM. The TEM micrograph of dried sample Cu/SiO_2 is shown in Figure 3. This figure confirms the formation of particles with average size of 150-200 nm.

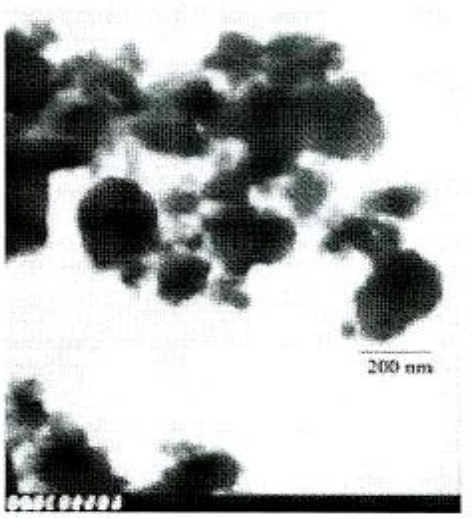

Figure 3.TEM micrograph of Cu/SiO_2 nanocomposite at 400°C.

The TEM micrograph of dried sampleCuO/SiO_2 is shown in Figure 4. This figure confirms the formation of particles with average size ranging 50-80 nm. Figure 5 presents the x- ray pattern of the A set of CuO/SiO_2 samples annealed at 200, 400 and 600°C. For the 200°C sample, the pattern corresponding to the copper nitrate is still presented as the partially hydrolyzed phase $Cu_2(OH).3(NO_3)$. Although the amount of the copper nitrate added, is below the solubility limit, and all precautions were taken to dissolve it, but two states could occur during the thermal treatment of the gel which explains the later fact: the precipitation of the compounds or separated ions lead to formation of compounds during annealing.

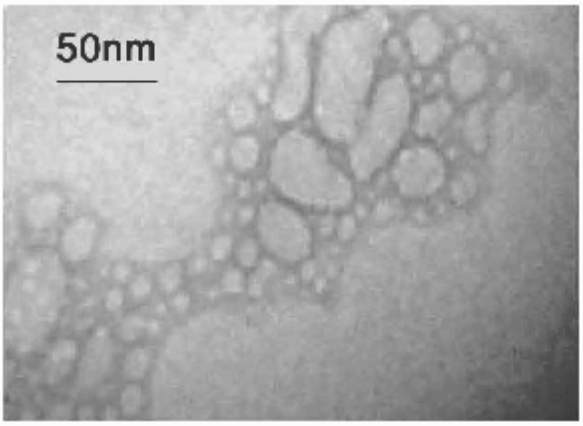

Figure 4. TEM micrograph of CuO/SiO_2 nanocomposite at 400 °C.

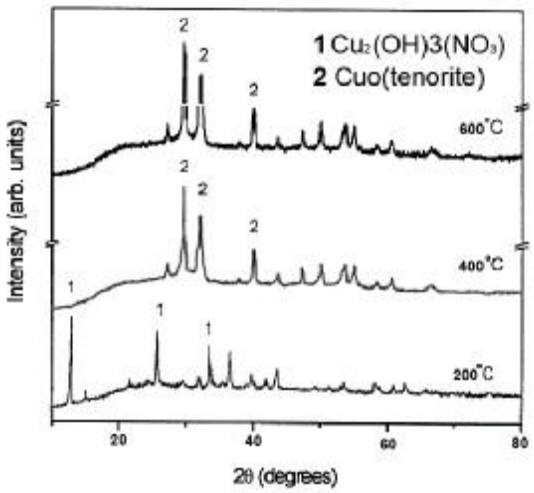

Figure 5. X-ray pattern CuO/SiO_2 sample annealed at 200, 400 and 600 °C.

For the samples annealed at 400 and 600°C, we can see the X-ray pattern corresponding to the CuO phase [17]. From the results, we can say that there is no evidence of the presence Cu_2O species in these samples.

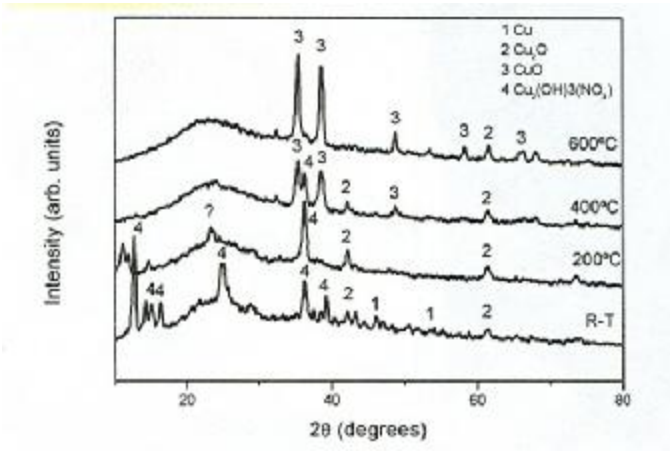

Figure 6. X- ray pattern of Cu/SiO_2 sample annealed at 200, 400 and 600 °C.

Figure 6 shows the x-ray results of the set of samples B, for the prepared sample it is possible to see a x-ray pattern with a lot of small peaks due to copper species such as; metallic copper, copper nitrate partially hydrolyzed and couprite oxide(Cu_2O). Sample B annealed at 200 ºC has the peaks corresponding to metallic copper, and partially hydrolyzed copper nitrate diminishes noticeably and Cu_2O peaks are predominant. For 400 ºC sample, we can almost observe peaks due to CuO and Cu_2O. Finally, at 600 ºC sample the peaks related to CuO are predominant and Cu_2O species have a very small contribution. From FTIR and X-ray results, we can conclude that in CuO/SiO_2 samples, there is formation of the Copper oxide particles mainly in form a ***Tenorite***. The evolution of copper species goes from copper nitrate to copper oxide species. The copper- particles doped samples (set B), the evolution is from Cu to Cu_2O, through an intermediate phase $Cu_2(OH).3(NO_3)$, and then, when nitric acid is used, it is converted to CuO. We have already mentioned, for both set A and B samples, there are differences for FTIR and XRD results. Both 980, 1078 cm^{-1} bands are separated from each other, whereas in B samples overlapping of these bands is evident. We can conclude that at these temperatures in set A samples copper is mainly incorporated into SiO_2 matrix as copper nitrate. There are no copper oxide particles, or the concentration is low. After copper nitrate is decomposed by thermal treatment, copper oxide particles are formed and interact with SiO_2 matrix via OH groups [18]. For set B samples, copper is incorporated to form particles or aggregates; copper particles are oxidized to form Cu_2O and CuO species depending on the thermal treatment.

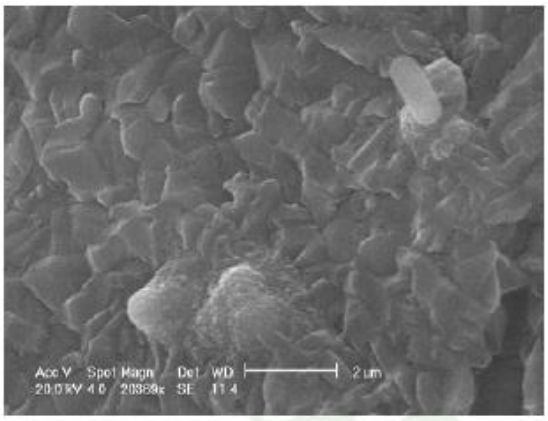

Figure 7. SEM micrograph of Cu-O particles on the silica matrix.

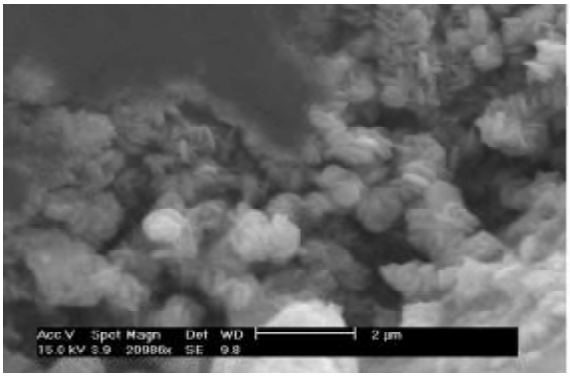

Figure 8. SEM micrograph of copper particles.

Scanning electron microscope (SEM) images of Figure 7 are used to study of sample morphology. At 200°C, we can see that the copper nitrate particles are embedded on the silica matrix. Increasing temperature to 400-800 °C causes copper nitrate

particles to decompose and convert to copper oxide particles that dope into silica matrix. SEM images show an inorganic polymerization that can form oxide network containing metal oxide clusters Cu-O. The exact composition of clusters depends on the annealing temperature and molar ratio of components. Figure 8 presents SEM micrograph of copper particles on the silica matrix with high porosity. The copper particles can be aggregated together and form nano-scale porosity with average pore size of about 150 nm.

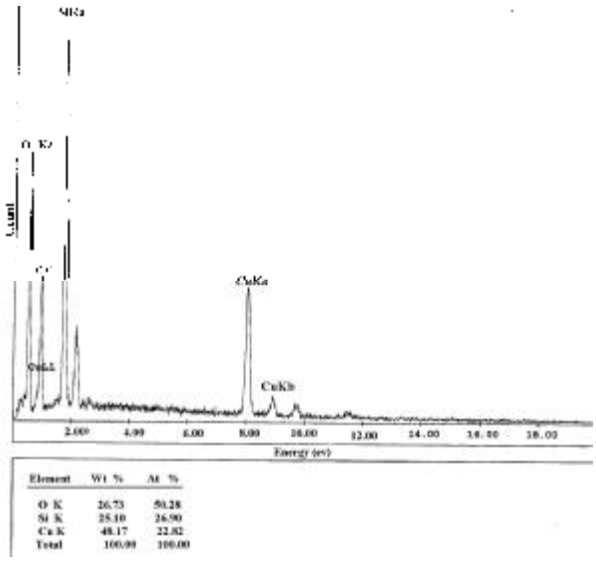

Figure 9. EDX of CuO/SiO_2 sample.

Figures 9 and 10 present chemical analysis as measured by electronic microprobe (EDX). This method of chemical analysis is a known method for fast elemental analysis of samples. Elemental analysis presents weight and atomic percent of oxygen, silicon and copper. Figure 8 shows the ratios of Cu/O (wt.%)=1.8, and Cu/Si (wt.%)= 1.91. This data confirms that the structure of clusters can be of the Cu-O-Si form. In figure 9, we can see ratio of Cu/O (wt.%)=4.75, Cu/Si (wt.%)=7.51, which shows that many copper particles have doped on the silica support with high porosity [17].

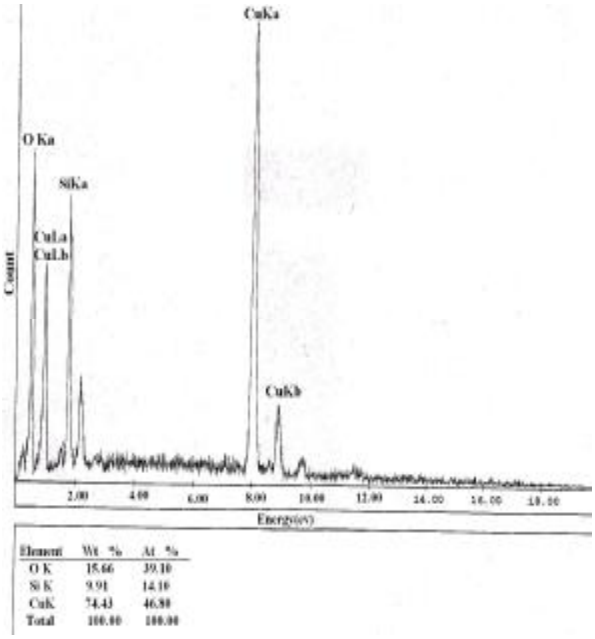

Figure 10. EDX of Cu particles on the silica matrix.

4. CONCLUSION

We have studied and compared nanostructures of copper oxide and copper based particles on the silica matrix. The exact composition of structures depends on copper source, molar ratio of components and annealing temperature. We can produce particles of metallic copper, cuprous and cupric oxide and compare these particles for synthesis method and characterization. Thus, their structures were analyzed by FTIR spectroscopy and XRD system at 200, 400 and 600 °C temperatures. We have recognized three main region contain Rocking (R), Bending (B) and Stretching (S) on their structure using FTIR spectrum. The SEM micrographs and chemical analysis were compared by EDX of Cu and CuO/SiO_2 together. Average size of particles was determined to be 150-200 nm for copper particles and about 50 nm for copper ions using TEM micrograph. These nanocomposites have excellent stability and useful applications [18].

5. REFERENCES

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