

PREPARATION AND STUDY OF MOLECULAR STRUCTURE OF COPPER IONS DOPED IN A SILICA XEROGEL MATRIX

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Abstract The silica xerogel is prepared using copper source; 0.02 mol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ that has been added to 1 mol TEOS (tetraethyl orthosilicate). The copper ions are doped to silica matrix by the sol gel method and determination of total molar ratio of components with a reported molar ratio of $\text{H}_2\text{O} / \text{TEOS}(\text{R}) = 6.2$. In this method, the acidity the of reaction (pH) depends on the catalyst type in the hydrolysis step and the molar ratio of $\text{H}_2\text{O} / \text{TEOS}(\text{R})$ that is studied with gelation time (tg). In this reaction, acidity varies between 2.4 and 3.5. Average size and molecular structure of this nanocomposite were analyzed using TEM, FTIR and XRD. Copper oxide can be produced from the decomposition of copper nitrate and is doped on the silica matrix by thermal treatment.

Key Words Sol Gel Process, Copper (II) ions, Xerogel Matrix

چکیده در این تحقیق نمونه های سیلیکا-زیروژل با به کارگیری ۰/۰۲ مول نیترات مس ۳ آب بازای ۱ مول تترا اتیل اورتوسیلیکات تهیه می شود. با استفاده از فرآیند سل ژل و با تعیین نسبت مولی کل اجزاء، یون های مس در بستر سیلیکا قرار گرفتند که نسبت مولی آب/ تترا اتیل اورتوسیلیکات برابر ۶/۲ تعیین گردید. اثرات محیط واکنش (اسیدیته) از طریق نوع کاتالیزور در مرحله هیدرولیز و نسبت مولی آب/ تترا اتیل اورتوسیلیکات با مدت زمان ژلایسیون بررسی گردید که در این واکنش بین ۲/۴ و ۳/۵ تغییر می کند. با استفاده از میکروگراف الکترون عبوری و طیف مادون قرمز با انتقال فوری و پراش اشعه ایکس اندازه ذرات و ساختار مولکولی نانوکامپوزیت آنالیز شد. همچنین مشاهده گردید که توسط واکنش حرارتی، اکسید مس در نتیجه تجزیه ذرات نیترات مس حاصل شده که به روی بستر سیلیکا قرار می گیرد.

1. INTRODUCTION

In recent years, inorganic nanocomposite materials have been fabricated by a sol gel method [1,2]. Inorganic nanocomposite materials are hybridic of inorganic compounds in which at least one of the phases is done at a nanometer scale level.

One of the key factors in the sol gel process is the linking of inorganic materials to inorganic networks by hydrolysis and polycondensation

reactions that lead to two original targets. At first, they can raise the properties of final network or can form the second network into initial inorganic network for curing the properties of compounds [2]. Sol gel technology is considered to be a simple but highly efficient method for the synthesis of materials at low temperature. The sol gel process is a wet chemical method in which a precursor with $\text{M}(\text{OR})_n$ structure leads to an inorganic network incorporated with metal oxide [3].

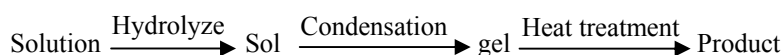


Figure 1. Total pattern of sol gel process.

This precursor can be the metal alkoxide of intermediate elements or a metal network such as Si that contains hydrolysable groups (OR), in which R is an organic group like methyl, ethyl and so on. These materials are converted to a gel network by an alkoxide reaction in the presence of water molecules and, finally, can be inverted into a solid state. There is an inorganic polymerization that can form oxide within the network containing metal oxide clusters of M—O—M [4]. Figure 1 shows the total pattern of sol gel process.

The initial solutions include metal alkoxide, solvent and a catalyst. Hydrolysis and condensation reactions lead to production of sol and finally the gel. Through thermal treatment, the gel is converted to powder, a thin film and porous materials. Metal-Silica nanocomposites can be produced by the sol gel method in which case they have particular properties. Through this method of preparation, metal ions can be doped into an ionic oxide network and converted to more stable compounds in comparison to other methods [5,6].

The sol gel polymerization of metal alkoxides in the presence of inorganic salts is led to form ceramic oxide materials that present important microstructure properties [7]. The original target of this investigation is doping copper species in Silica network under thermal treatment. In this a research, CuO/SiO₂ nanocomposites are prepared from a xerogel form by the sol gel method. We then annealed porous materials for the study of the molecular structure.

2. EXPERIMENTAL DETAILS

In this investigation, the raw materials containing Tetraethyl orthosilicate (Fluka, 98%) (TEOS), Ethanol absolute (Merck) (ETOH), copper nitrate tri-hydrated (Merck), HNO₃ (Merck, 65%),

CH₃COOH (Merck, 99-100%) were used with the mentioned specifications. Two samples of CuO/SiO₂ nanocomposite xerogel were produced by the sol gel method, and one was prepared as a blank sample. The Initial solution for CuO/SiO₂ xerogel was fabricated through a mixture of TEOS, H₂O, ETOH, Cu(NO₃)₂.3H₂O, 3M HNO₃, 4M CH₃COOH, with total molar ratio of TEOS: ETOH: H₂O to 1:1.3:6.2. Then, 0.02 mole of Cu(NO₃)₂.3H₂O, 0.005mole of 3M HNO₃, 0.004 mole of 4M CH₃COOH were added to 1mole of TEOS for canalization of a hydrolyze condensation reaction. Then the solution is mixed by a magnetic stirrer for 2.5 hours until a homogeneous solution is formed.

After this, the solution is acidity (pH) is measured by a pH-meter (reported ph 2.4). The solution is kept in a closed container (25-30 °C temperature). The soft gel changed to a dark- blue color after 84 hours (3.5 days) through a gelation treatment. The gel samples are dried in an oven in an air atmosphere at about 200 °C for 2 hours until the gelation is completed. For the next sample, we anneal a small amount of wet gel in an electrical furnace at 600 °C for 30 minutes until the condensed nanocomposite was produced. The blank solution is prepared without the addition of Cu(NO₃)₂.3H₂O with a molar ratio ETOS, ETOH, H₂O to 1:1.3:7.4. Then HNO₃, and CH₃COOH were added as catalysts and the solution is mixed for 3.5 hours in an ambient temperature by a magnetic stirrer until a homogeneous solution is formed (pH = 3.5). The solution is kept in a closed container (25-30 °C) for 120 hours in which time the gelation will be completed. The colorless soft silica gel is put into an oven, in air atmosphere, at 180 °C for 40 minutes and the other blank sample is kept in a ambient media in a closed container for 96 hours for the drying. Process for analysis of the product, the samples are put into an oven at a

desired temperature for 25 minutes in atmospheric conditions, then are grounded to form powder samples.

The infrared spectra was measured in a FTIR spectrometer of a Genesis system- model (ATI), using a 0.05 gr of powder sample with 0.3 gr of KBr. TEM micrograph was obtained on a TEM instrument, Phillips system-model Em208S, operating at 100 kV power. The dry samples were suspended in dry cyclohexane, and sonicated for 1-2 minute. Then the solution was allowed to settle and a droplet of the resulting supernatant was placed on a holey carbon film and dried. The x-ray diffraction (XRD) patterns were registered in a Philips instrument using PW 1800 Diffractometer and the radiation of a copper Anodic Tube $\lambda = 1.54\text{\AA}$.

The PH was measured by an Omega PH meter-model 744. The condensation of samples was done in an Oxaiton heat furnace with a high thermal capacity (1500°C).

3. DISCUSSION

The sol gel process contains three major steps, Hydrolysis, Polycondensation and Thermal treatment. In each step, chemical reactions and individual physical variations are completed.

3.1. Hydrolysis In this step, water reacts with TEOS and hydroxyl groups are replaced by

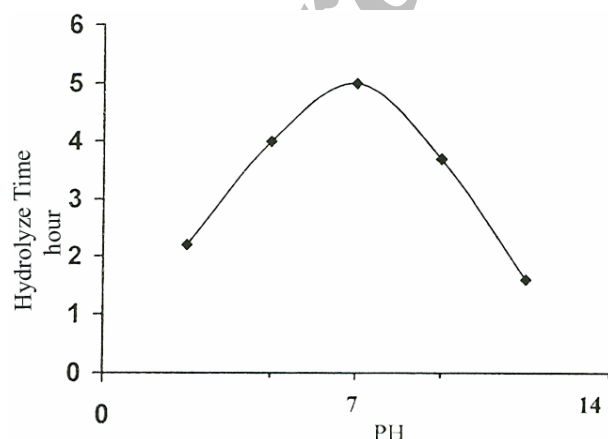
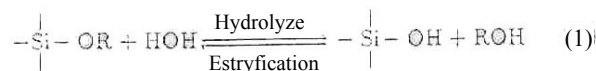


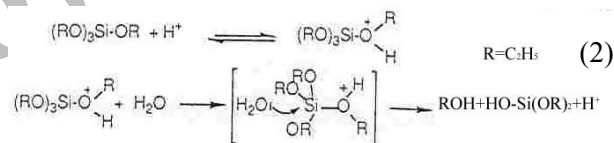
Figure 2. The variation of pH to hydrolysis time.

alkoxide groups (1).



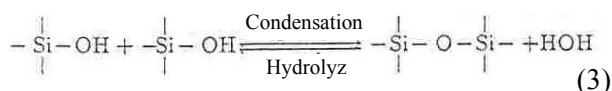
This substitution can be completed to prepare colloidal particles at nanometer scale. The hydrolysis of TEOS is a spontaneous reaction and factors like; metal charge, the size of alkoxy group, temperature, PH and water content affect time or velocity of the hydrolysis. Figure 2 shows the PH variations in hydrolysis time [9].

In case of a Silica xerogel formation, relations between the acidity of solution and the hydrolysis time of the reactions has been presented at pH=7, which hydrolysis constant reach to lowest limit. Reaction time increases and with changes in pH=7, the velocity of hydrolysis raises and reaction time reduces. For increasing the velocity of hydrolysis, we can use acidic or alkali catalysts. In the case of alkoxysilanes it is well known, that mechanism (2) is the best method for the first step of the sol gel process [9].



The mechanism consists of a nucleophilic attack of water molecules on the Silicon center this mechanism is dependent on the type of catalyst. In this research, using an acidic catalyst, the first step is to contain reversible protonation of alkoxy groups that lead to better leave alkolic groups (2). The nucleophilic substitution with water molecules leads to 5 coordinates intermediate formations [9].

3.2. Condensation In this step, the hydrolyzed species of Silanol ($\text{Si}-\text{OH}$) react together to form Siloxane bridges $\text{Si}-\text{O}-\text{Si}$ (3). The preparation of these bridges lead to a cancellation of alcohol or water molecules[10].



Continuation of this reaction leads to the formation

TABLE 1. Relation R to Gelation Time (tg).

R	0.6	1.2	3	3.8 -4	5	6.2	7.4	10
Time (Day)	6	4	1.7	1.5	2	3.5	5	5.7

of a polymeric network which the soft gel is prepared from. In condensation, the molar ratio of H_2O : TEOS (R) and the type of catalyst affect the structure and formation velocity of the polymeric network. Table 1 shows the molar ratio of H_2O : TEOS (R) to gelation time. In this study, the gelation time in $R = 6.2$ days for CuO/SiO_2 xerogel, and $R = 7.4$ days for Silica xerogel to the pure form were compared. Figure 3 shows the variations of R to the gelation period (tg), and it shows after $R = 3.8-4$, raising R, the gelation time will increase.

Also Figure 3 presents $R = 3.8-4$, the gelation

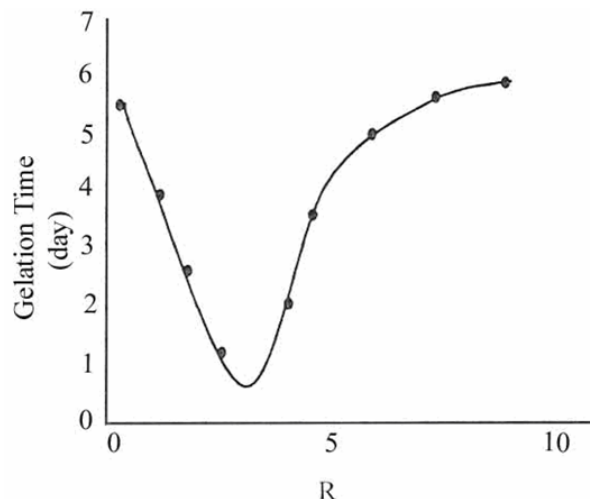


Figure 3. The curve of gelation time variation to molar ratio H_2O /TEOS (R).

period reaches its lowest pear. After this range, ($R > 4$) with an increase in pore size and a decrease

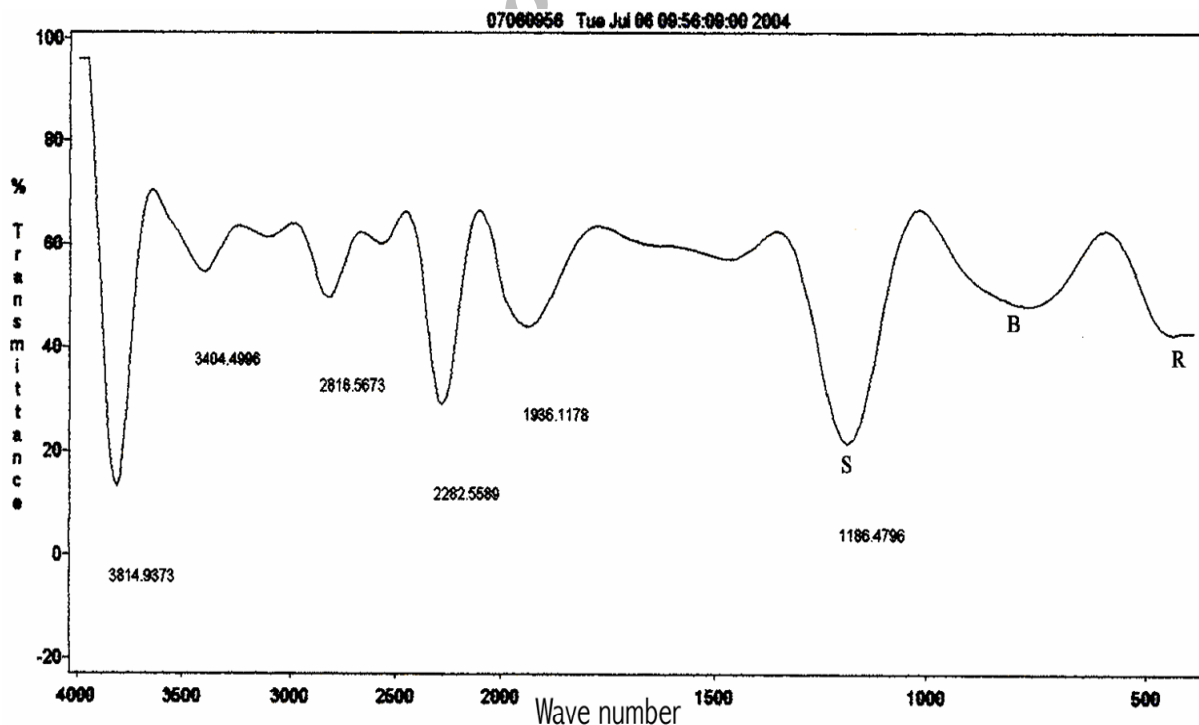


Figure 4. FT. IR spectra of CuO/SiO_2 nanocomposite.

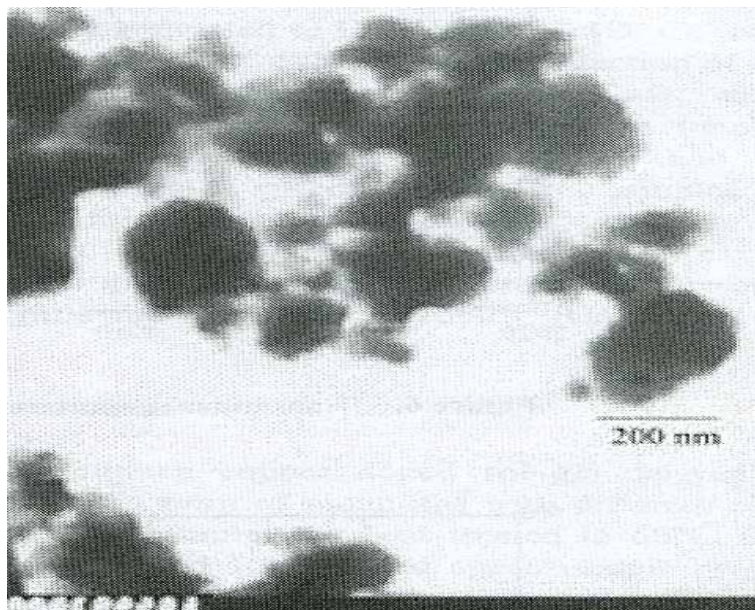


Figure 5. TEM micrograph of CuO/SiO₂ nanocomposite.

of their number, the gel structure varies [10].

3.3. Thermal Treatment The thermal treatment is done in two steps. In the first step of drying, the solvent is done through evaporation by a soft thermal treatment at 200 °C after which a dry/drying gel is formed. In the next step, at temperatures between 600-1000 °C, the organic materials decompose. The properties of the sol gel production depend on how the thermal treatment and its conditions are performed. Sometimes these effects are interviewed in the velocity of solvent vaporization and its influence on polymeric network. The vaporization of solvent is the caused due to intense contraction in the gel structure of CuO/SiO₂ nanocomposite at room temperature. Finally, CuO/SiO₂ is prepared the xerogel form [10].

4. RESULTS

The bonding and molecular structure study of the CuO/SiO₂ nanocomposite was done in bonding

the vibrational mode through FTIR spectra. Figure 4 shows the FTIR transmittance spectra in the range of 500-4000 Cm⁻¹ media for SiO₂:CuO in a powder form.

Each of three major features are related to transversal optical (TO) absorption bands the shown in the Figure 4 which can be characterized in terms of particular vibration mode of the Oxygen (O) atom in relation to the bridging of the Silicon (Si) atom. Rocking (R) of the (O) atom about an axis by two Si atoms characterize the vibrational behavior of the lowest frequency to bond central at 475-490 Cm⁻¹. Bending (B) of the (O) atom along a line bisecting the axes was formed by the two Si atoms characterizing the vibrational mode of the middle TO band centered at 780 Cm⁻¹ [11].

The remaining TO band and its high frequency 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 [10,12]. The main band of the SiO₂ FTIR spectra is correspondent with the asymmetric stretching (S) mode at 1186 Cm⁻¹, however its presence at 1150-1250 Cm⁻¹ it is not clear. It has

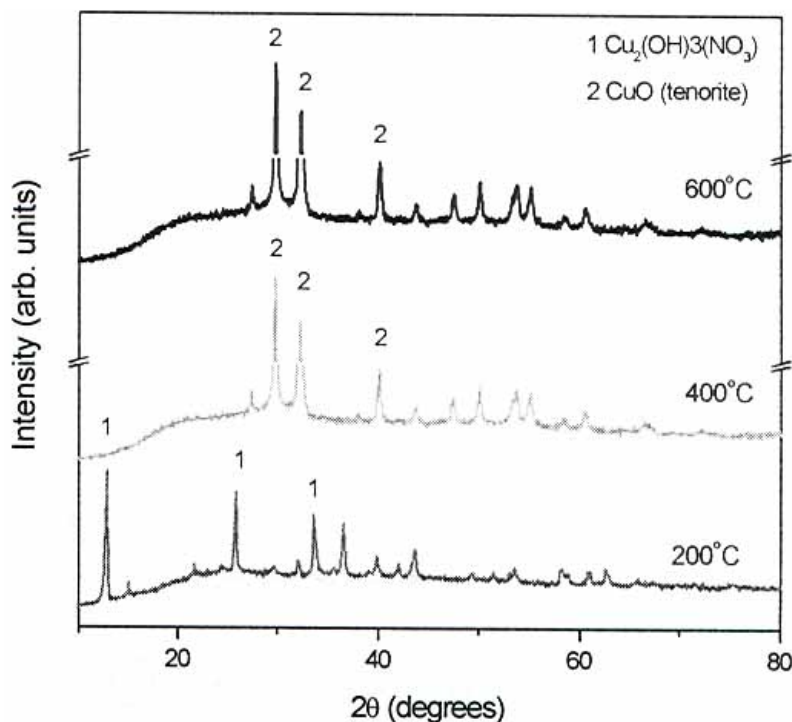


Figure 6. X-ray pattern of CuO/SiO₂ sample annealed at 200, 400 and 600°C.

been reported the FTIR spectra this final part should be rewritten, in the frequency range of 1150 to 1250 cm^{-1} , has an amplitude comparable or bigger than the main stretching band at 1186 cm^{-1} [13,14]. This has been achieved in vitreous SiO₂ samples prepared by the sol gel method using specific preparation conditions. Also from Figure 4, we can observe the band at 850-990 cm^{-1} assigned to the vibration of the [Si—OH] groups, this band shows a noticeable evolution with the annealing temperature. In Figure 4, we have an overlap of this band and bending band of Si—O (B) that observed to spread peak type and lead to shoulder in vibrational of bending frequency Si—O (S) [15].

The absorption at the range of 1900-2300 cm^{-1} related to the nitrogen intermediate compositions produced in the decomposition of copper nitrate to copper oxide. The low absorption band at the range of 1450 cm^{-1} is the factor of reduction nitrate groups in the solution that presents complete decomposition of these groups and confirm the

validity of molar ratio copper nitrate tri-hydrated in sol gel solution. The absorption band $\text{C}_2\text{H}_5\text{—O—}$ appears at 2816 cm^{-1} , and a vibrational range of 3404 cm^{-1} corresponding with the intermolecular structure and the O—H band

there is the absorption band corresponding to H₂O in solution at 3814 cm^{-1} range with a low shift [16]. The TEM micrograph of an dried sample CuO/SiO₂ was shown in Figure 5, this Figure confirms the formation of average size 200 x 150 nm².

Figure 6 presents the x- ray pattern of CuO/SiO₂ 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 $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$.

Although the amount of the copper nitrate added, is below the limit of solubility and all precautions were taken to dissolve it, but two states could occur during the thermal treatment of the gel which explain the later fact: the precipitation of the compounds or the separation of ions which leads to

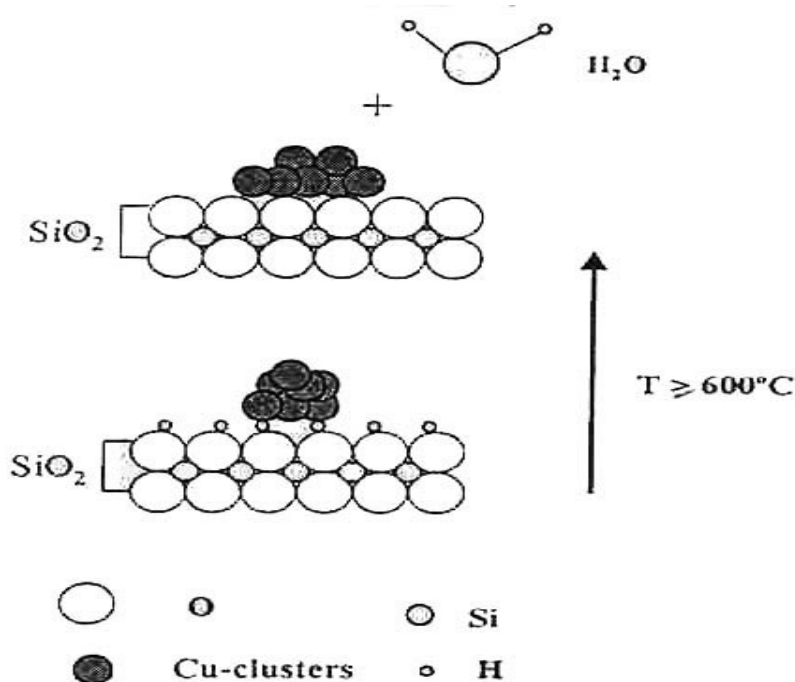


Figure 7. Schematic representation of the metal-glass interaction via hydrogen atoms.

the formation of compounds during annealing. For the 400 and 600 °C samples, we can see the X-ray pattern corresponding to the CuO phase [17]. From this, we can say that there is no evidence of the presence Cu₂O species in these samples.

Figure 7 shows that we can illustrate how the metal-glass interact via a hydrogen atom located at the 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 in direct contact with the oxygen atoms of the support network.

5. CONCLUSIONS

From the FTIR and X-ray results, we can conclude that for CuO/SiO₂ samples, there is a formation of the copper clusters mainly in form of Tenorite.

The evolution of the copper species goes from copper nitrate to copper oxide. 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 FTIR results; it is well known that the band at 850- 990 Cm⁻¹ is attributed to the Si—OH groups. The FTIR results show that the copper ions are mainly incorporated into the SiO₂ matrix as copper nitrate, copper oxide (CuO) particles or their concentration remains low. After the copper nitrate decomposition is carried out, the copper oxide (CuO) particles are formed and they interact with the SiO₂ matrix via OH groups. It is believed, there is a correlation between the existence of metal oxide particles embedded into the SiO₂ matrix and the overlapping of the silanols and Si-O stretching bonds. This overlapping might be associated to the interaction between the gust particles and the

matrix host [18].

Copper clusters have been studied based on their particles. The exact composition of clusters depends on annealing temperatures. By thermal treatment and choosing the appropriate copper source, cupric oxide can be produced. These nanocomposite metallic clusters have an excellent stability and reproducibility. By FTIR absorption, the interaction of the metal based species and Oxide support can be studied.

6. REFERENCES

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