Egypt. J. Chem. **53**, No. 4, pp. 497-514 (2010)

Preparation and Characterization of Nano Cu and CuO Catalysts Supported on Washcoated Cordierite

M.M. Selim[a]*, S.A. Hassan[b], M.R.A. Rezk[c] and N.M. Deraz[a,d]
[a]Department of Physical Chemistry, National Research Center, [b]Department of Chemistry, Faculty of Science, Ain Shams University, [c]Ministry of Scientific Research, Cairo, Egypt and [d]Department of Chemistry, College of Science, King Saud University, Saudi Arabia.

NANO copper and copper oxide supported on Al_2O_3 washcoat deposited on cordierite was prepared by mild reduction method using hydrazine hydrate as reducing agent in non-aqueous media. The effect of loading (5 and 10% Cu), calcination temperature 500, 600 and 700 ^oC on the formed nano CuO was investigated. The preheated samples were characterized by X-Ray diffraction (XRD) and scanning electron microscope (SEM). The results indicated that, 5wt.% (Cu/Al_2O_3)/cordierite has the less crystallite size and the smallest crystallite size of CuO was observed in case of 5wt.% (CuO/Al_2O_3)/cordierite calcined at 500^{o}C for 1hr.

Keywords: Nano , Cu , CuO , Cordierite, Al_2O_3 and Washcoat**.**

Metallic and metal oxide based nanoparticles have received significant attention by researchers due to their unique properties such as color, conductivity, melting temperature, magnetism, catalytic, specific heat and light absorption in comparison with bulk metal(1-5).

Nano Cu and CuO particles have attracted much attention of researchers due to their applications in catalysis(6). In other words, copper nano particles show much higher specific catalytic efficiency than bulky copper due to their enormous surface area(7). Many techniques such as radiation methods(8), micro emulsion techniques(9-11), super critical techniques(12), vacuum vapor deposition(13) and chemical reduction(14-15) have been developed to synthesize copper and copper oxide nano particles. Such catalysts are essential for technological advances in environmental protection, improving indoor air quality, and in chemical synthesis and processing.

---

*Corresponding author E-mail: mmaselim@yahoo.com

Copper oxide based catalysts have been extensively examined as a possible substitute for noble metal catalysts, because they have much lower cost and comparable or even higher activity for CO oxidation(16-20). Several kinds of supports, including metal oxides, zeolites, mesoporous silicas, cordierite, carbons and others, have been used for preparing the copper oxide based catalysts(19-24).

The most widely used ceramic material as catalyst carriers in conversion reactions of the noxious emission gases to harmless ones is cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$. Cordierite has a set of unique properties including low thermal expansion coefficient, excellent thermal shock resistance, low dielectric constant, high volume resistivity, high chemical durability, high refractoriness and high mechanical strength. Therefore, they are widely used, as substrate material for integrated circuit boards and as refractory materials (25-30).

The limited use of cordierite as a catalyst support is due to the fact that the small specific surface area ($S_{BET}< 1m^2/g$) may decrease the dispersion of active metals. To increase the specific surface area, cordierite is coated with a material of high surface area called the washcoat, which acts as a host for metal catalysts. The washcoat material on cordierite for catalytic purpose should possess a variety of properties such as high surface area, appropriate pore structure and thermal stability. A material that combines these properties and is mostly used in these applications is alumina(31). The washcoat is usually applied on the cordierite by impregnation of the cordierite in a suspension (slurry) of the powder and subsequent drying and calcination(32).

In this paper nano Cu and CuO supported on washcoated cordierite were prepared. The preparation assembly is comprised of three basic parts as shown in Fig. 1. The first one is the substrate (the base), which is ceramic (cordierite) and the surface of this substrate is coated with a layer of a high surface area material called the washcoated (alumina). Finally, within the matrix of the washcoated, the transition metals and oxides (Cu and CuO) are dispersed.

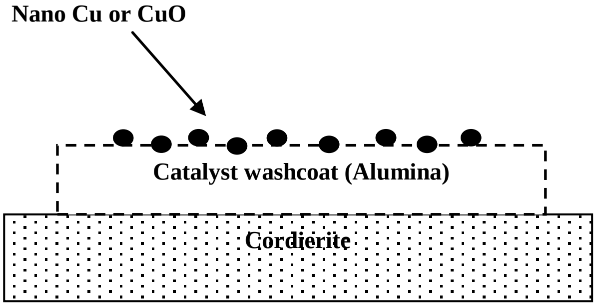

Fig. 1. A cartoon of nano Cu or CuO supported on washcoated cordierite.

Experimental

Materials used

Copper nitrate (Merck**)**, sodium hydroxide (Laboratory Rasayan), ethylene glycol (Merck), hydrazine hydrate (Merck), cordierite (prepared from Egyptian kaolin and talc), $Al(NO)_3$ (Merck), ethyl alcohol (Laboratory Rasayan) and acetone (Laboratory Rasayan).

Preparation of Al_2O_3 washcoat on cordierite by impregnation

A given mass of a finely pellet cordierite $Mg_2Al_4Si_5O_{18}$ (prepared from talc and kaolin) was impregnated with solutions containing different concentration of aluminum nitrate , the loading of alumina was determined by weighting where the different concentrations of aluminum nitrate were used in order to obtain the nominal compositions of 5 wt.% of Al_2O_3. Then it was dried at 100^oC over night and calcined at 550^oC for 3 hr to obtain a well-adhered washcoated layer of 5 wt.% of alumina upon the cordierite.

Preparation of nano Cu and CuO supported on washcoated cordierite

A previously prepared 5 wt.% (Al_2O_3)/cordierite was impregnated with aqueous solution of copper nitrate. The different concentrations of copper nitrate were used in order to obtain the nominal compositions of 5 and 10 wt% Cu /Al_2O_3/Cordierite. The supported copper nitrate precursors on cordierite were dried at 100^oC then introduced in the reaction flask at 80^oC with a mixture of ethylene glycol, hydrazine hydrate solution (80%) and sodium hydroxide (pH of solution 11-13) after steering for about 10 min a black solid of copper metal supported on cordierite was obtained. At the end of the reaction the copper supported on cordierite samples was separated from the solution and washed with alcohol and acetone several times and dried at 80^oC.

Nano copper oxide from copper supported on washcoated cordierite, 5 and 10 wt% CuO/Al_2O_3/cordierite obtained by calcination of previously prepared nano copper supported on washcoated cordierite in open air at different temperatures 500, 600 and 700^oC for 1 hr.

Techniques

X-ray diffraction (XRD) analysis was performed on (Bruker D8 diffractometer with Cu-kα radiation (λ=1.54 Ǻ) at 40 kV and 40 mA. The average crystallite sizes of Cu and CuO phase were calculated from the line broadening according to Scherrer equation⁽³³⁾

$$d = K\, \lambda / B_{1/2} \cos\theta$$

where, d is the mean crystallite diameter , λ is the x-ray wavelength, K is the Scherrer constant (0.89) , $B_{1/2}$ is the full width at half maximum (FWHM) of the different peaks of Cu and CuO and θ_B is the diffraction angle.

Scanning electron microscopy (SEM) was taken on (Philips XL30); the samples were first sputtered with a thin layer of gold to avoid charging.

Results and Discussion

Status of Al_2O_3 washcoat on cordierite

From the obtained XRD analysis (Fig. 2) it is seen that, only the patterns of cordierite were observed, no patterns related to alumina were detected.

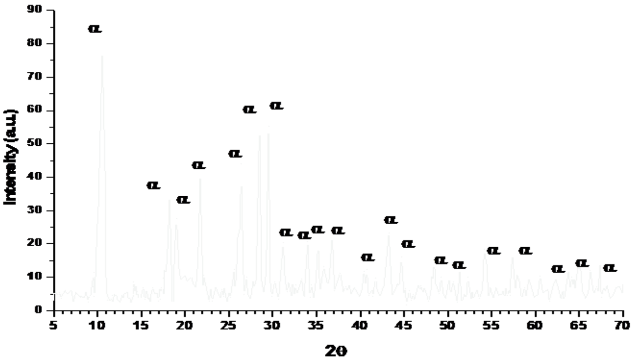

Fig. 2. XRD pattern of cordierite coated by 5 % Al_2O_3 preheated at 550^oC for 3 hr soaking time (α = Cordierite).

Scanning electron microscope (SEM) photographs of 5 wt. % Al_2O_3 washcoat on cordierite calcined at 550°C for 3 hr at different magnifications are illustrated in Fig. 3. From the surface view of washcoated, it can be seen that a well-adhered washcoat layer of alumina formed on the irregular cordierite surface. Based on the results from XRD and SEM, it can be concluded that cordierite has been successfully coated with alumina.

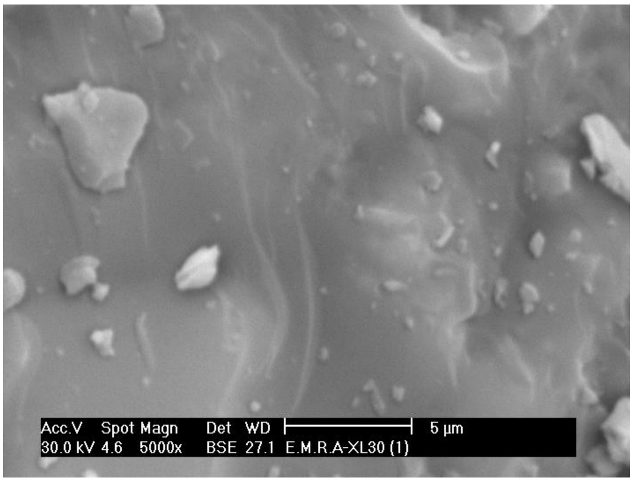

Fig. 3-a. SEM images of cordierite before coating with alumina at magnification 5000 x.

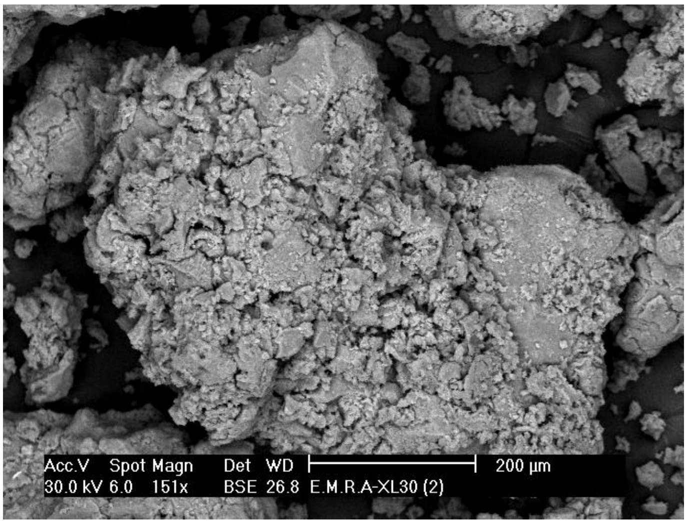

Fig. 3-b. SEM images of cordierite coated with 5wt.% preheated at 550°C for 3 hr soaking time at magnification 151x.

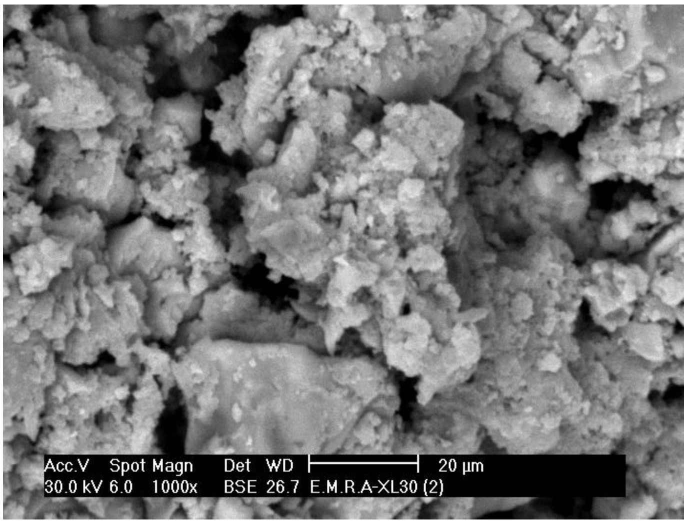

Fig. 3-c. SEM images of cordierite coated with 5wt.% preheated at 550°C for 3 hr soaking time at magnification 1000x.

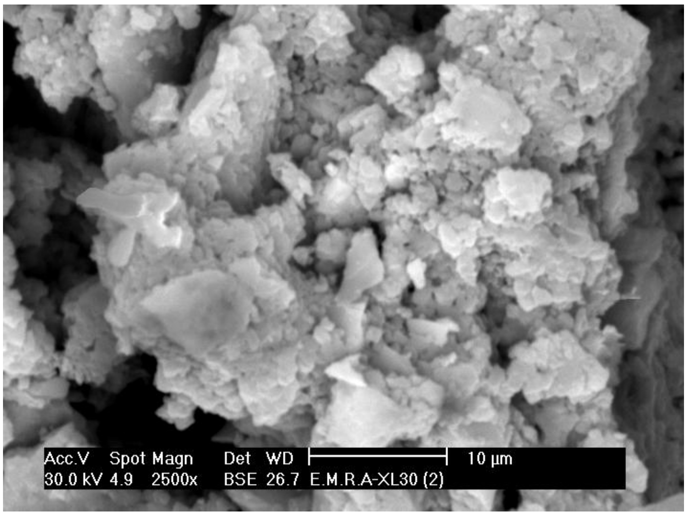

Fig. 3-d. SEM images of cordierite coated with 5wt.% preheated at 550°C for 3 hr soaking time at magnification 2500x.

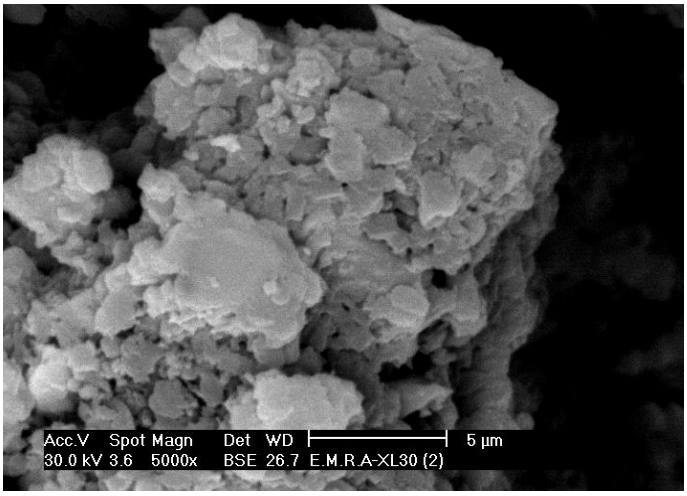

Fig. 3-e. SEM images of cordierite coated with 5wt.% preheated at 550°C for 3 hr soaking time at magnification 5000x.

Nano Cu and CuO supported on washcoated cordierite

Nano copper was prepared by reduction of copper nitrate with hydrazine as a reducing agent in non aqueous solution. The mechanism of the reaction of Cu^{+2} ions with hydrazine molecules in neutral and basic environments can be expressed as follows(34).

$$Cu^{+2} + N_2H_2 = Cu\downarrow + N_2\uparrow + 2\ H^+$$

It is known that, the metal forms complex with hydrazine at ambient temperature(35), this complex $(Cu(N_2H_2)_3)^{2+}$ is very stable in alkaline system at room temperature, but with increasing temperature the stability of this complexes decreases and decomposes to form pure nano copper metal(36).

Figures 4-11 show the XRD diffractograms of supported Cu and CuO on washcoated cordierite. The X-ray data allow to investigate the effect of loading with 5 and 10 wt.% of copper and its oxide supported on washcoated cordierite and calcination temperature of CuO on the crystallinity and crystallite size of copper metal and copper oxide phases. The peak height of [111] and [111] lines (main diffraction peaks of Cu and CuO, respectively) was considered as a measure of their crystallinity, according to the different loading on washcoated cordierite. The intensity of peaks of copper metal and its oxide were found to be in the following order; 5% <10%. This order corresponds to an increase of the CuO and crystallite size. The crystallite size calculated by Scherrer formula increases by increasing calcination temperature in the order 500°C < 600°C < 700°C (Table 1).

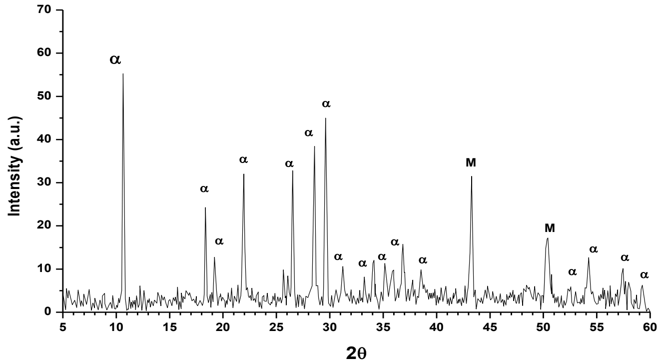

Fig. 4. XRD pattern of 5 wt.% Cu supported on washcoated cordierite (α = Cordierite, M = Cu).

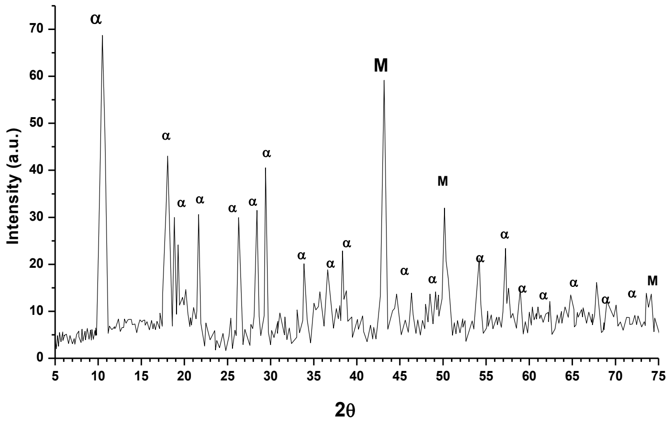

Fig. 5. XRD pattern of 10 wt. % Cu supported on washcoated cordierite (α = Cordierite, M = Cu).

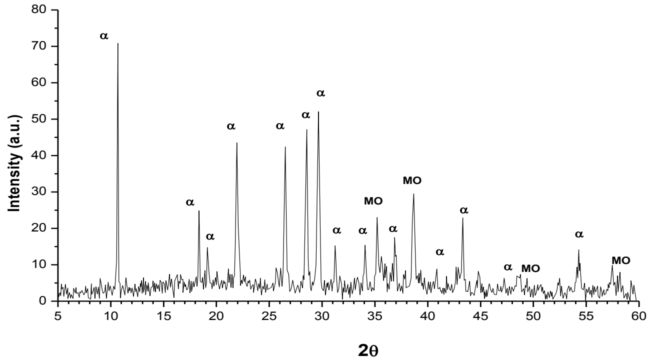

Fig. 6. XRD pattern of 5 wt. % CuO supported on washcoated cordierite calcined at 500 °C for 1hr soaking time (α = Cordierite, MO = CuO).

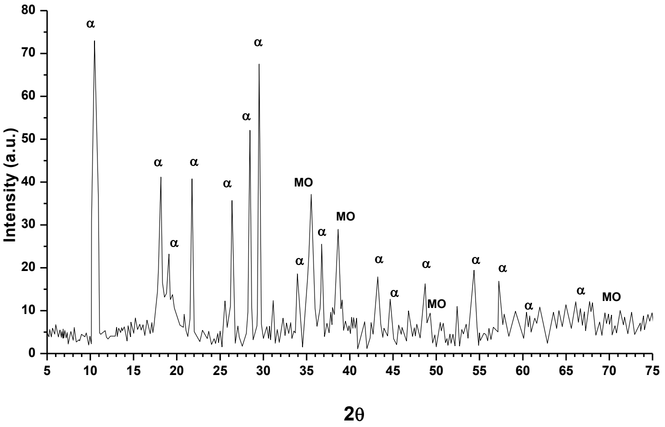

Fig. 7. XRD pattern of 10 wt. % CuO supported on washcoated cordierite calcined at 500 °C for 1hr soaking time (α = Cordierite, MO = CuO).

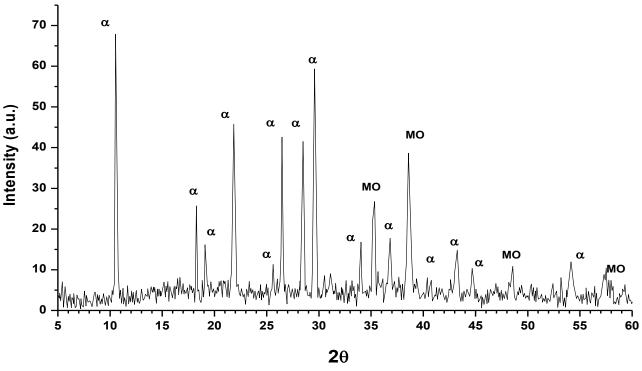

Fig. 8. XRD pattern of 5 wt. % CuO supported on washcoated cordierite calcined at 600 °C for 1hr soaking time (α = Cordierite, M = Cu).

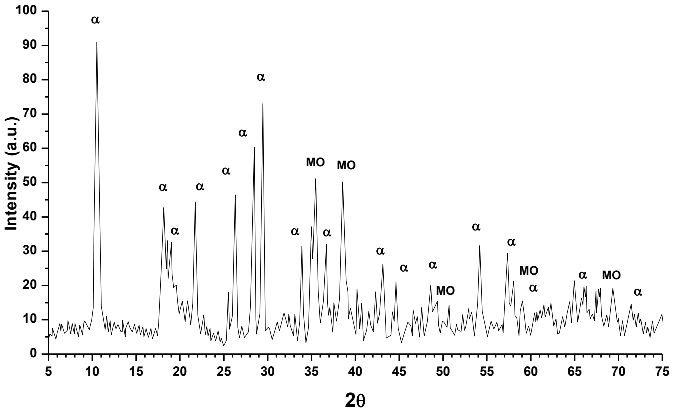

Fig. 9. XRD pattern of 10 wt. % CuO supported on washcoated cordierite calcined at 600 ^{o}C for 1hr soaking time (α = Cordierite, MO = CuO).

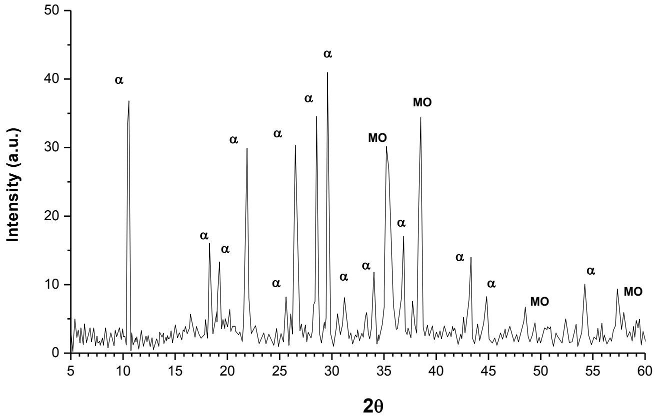

Fig. 10. XRD pattern of 5 wt. % CuO supported on washcoated cordierite calcined at 700 ^{o}C for 1hr soaking time (α = Cordierite, MO = CuO).

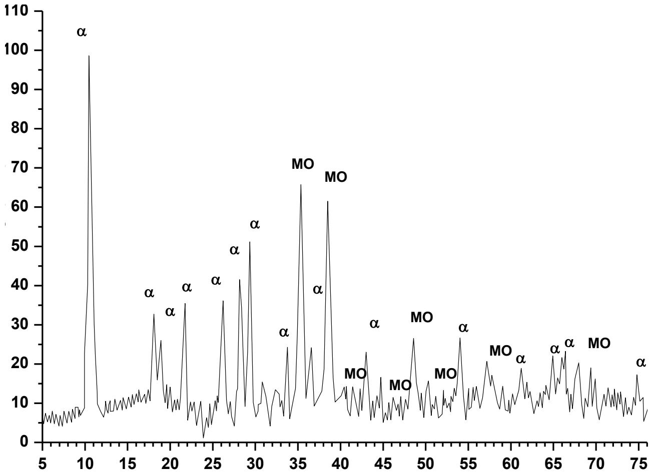

Fig. 11. XRD pattern of 10 wt. % CuO supported on washcoated cordierite calcined at 700 ^{o}C for 1hr soaking time (α = Cordierite, MO = CuO).

TABLE 1. Crystallite size of different Cu and Cu oxide.

Sample	**Calcination Temperature (^{o}C)**	**Crystallite size (nm)**
5 wt.% Cu/ Al_2O_3 /cordierite	**-**	**5.6**
10 wt.% Cu/ Al_2O_3 /cordierite	**-**	**7.4**
5 wt.% CuO/ Al_2O_3 /cordierite	**500**	**6**
10 wt.% CuO/ Al_2O_3 /cordierite	**500**	**9**
5 wt.% CuO/ Al_2O_3 /cordierite	**600**	**7.2**
10 wt.% CuO/ Al_2O_3 /cordierite	**600**	**14**
5 wt.% CuO/ Al_2O_3 /cordierite	**700**	**18.6**
10 wt.% CuO/ Al_2O_3 /cordierite	**700**	**16.2**

Scanning electron microscope images (Fig.12,13) show homogenous dispersion of Cu supported on washcoated cordierite. CuO supported on washcoated cordierite was homogenously dispersed after calcination and the crystallite size was found to be in nano scale based on x-ray data.

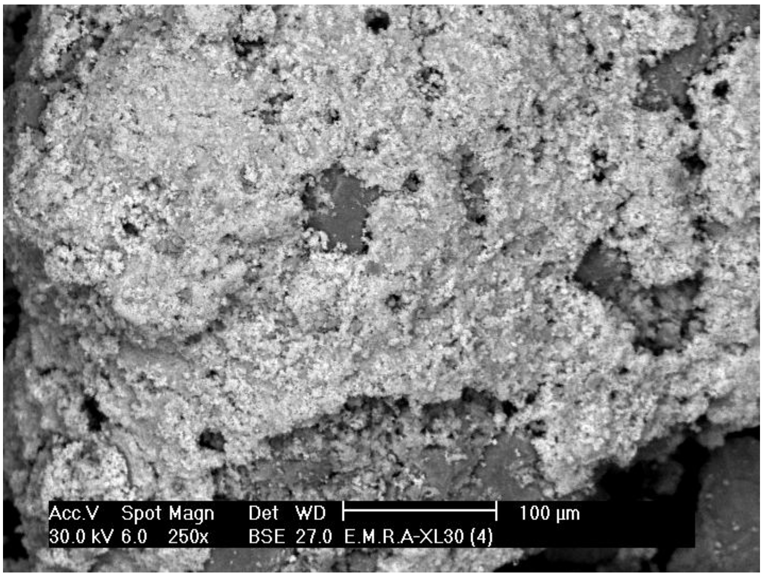

Fig. 12-a. SEM images of nano 10 wt. %Cu metal supported on washcoated cordierite at magnification 250x.

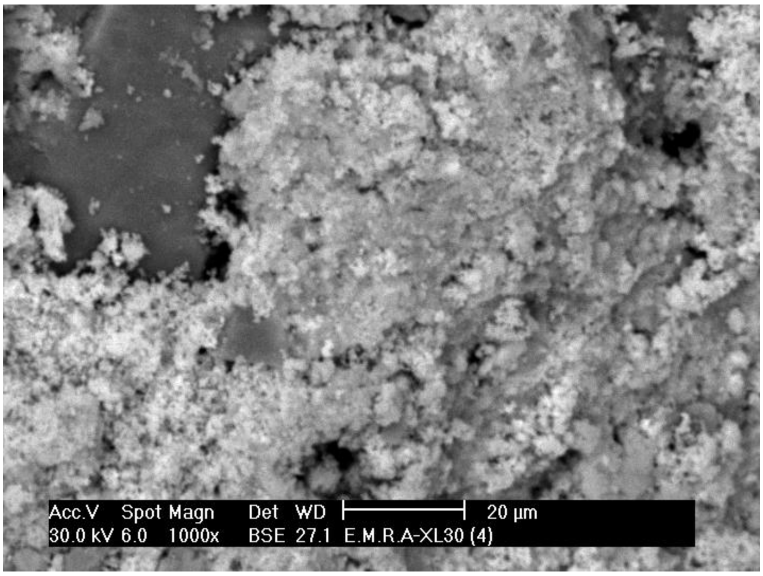

Fig. 12-b. SEM images of nano 10 wt. %Cu metal supported on washcoated cordierite at magnification 1000x.

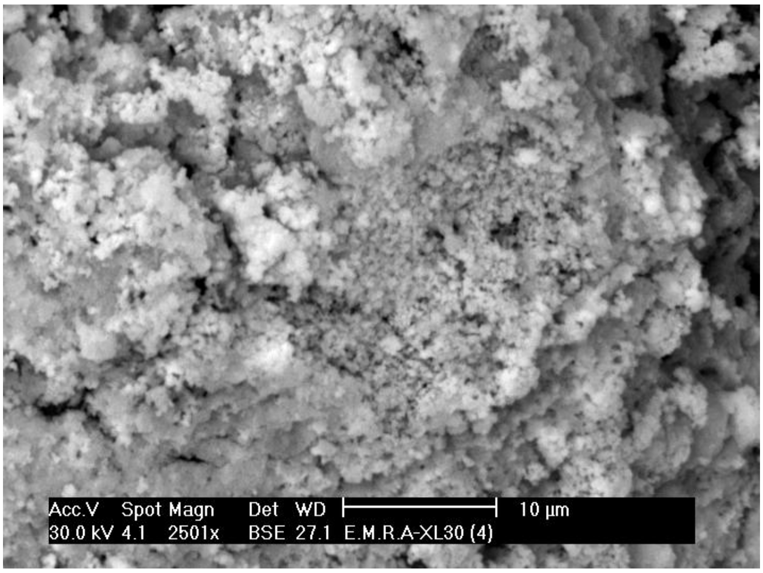

Fig. 12-c. SEM images of nano 10 wt. %Cu metal supported on washcoated cordierite at magnification 2500x.

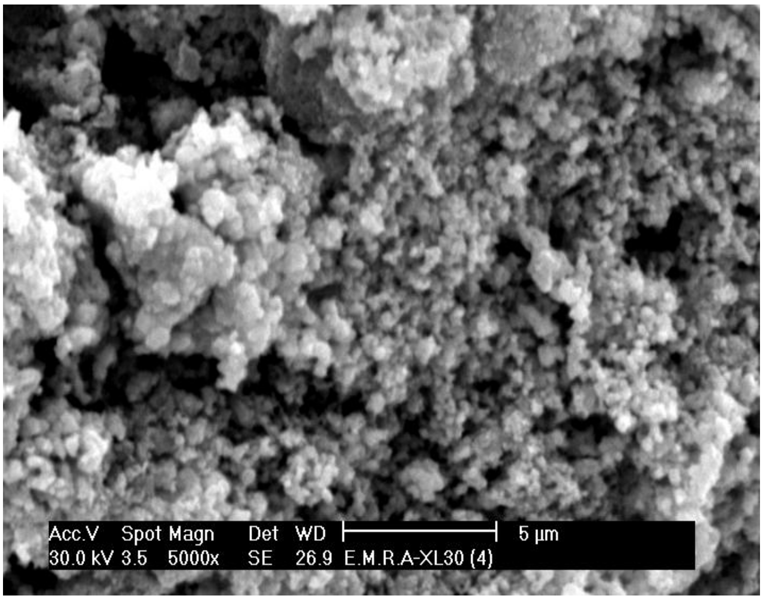

Fig. 12-d. SEM images of nano 10 wt. %Cu metal supported on washcoated cordierite at magnification 5000x.

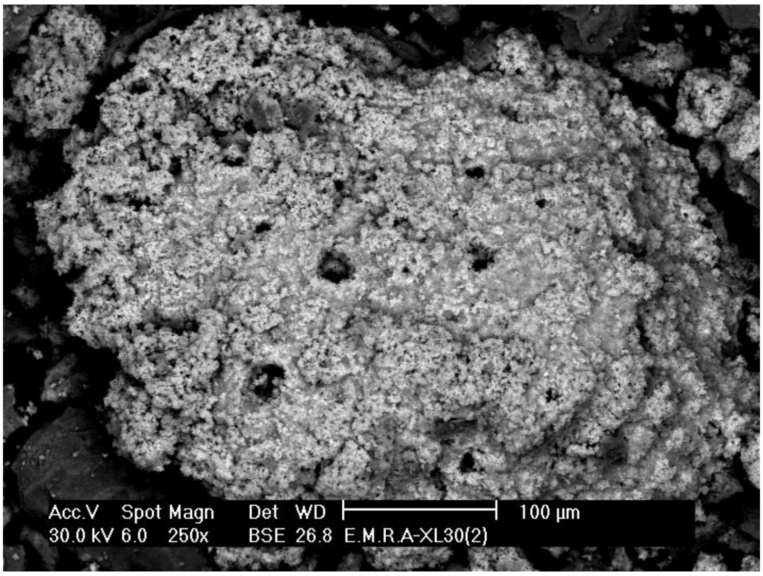

Fig. 13-a. SEM images of 10 wt. % CuO supported on washcoated cordierite calcined at 500 ^{o}C for 1hr soaking time at magnification 250x.

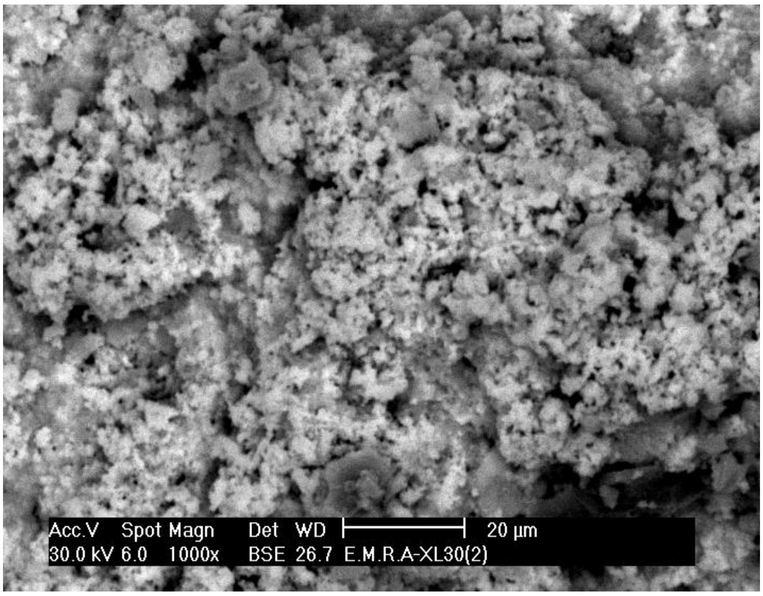

Fig. 13-b. SEM images of 10 wt.% CuO supported on washcoated cordierite calcined at 500 ^{o}C for 1hr soaking time at magnification 1000x.

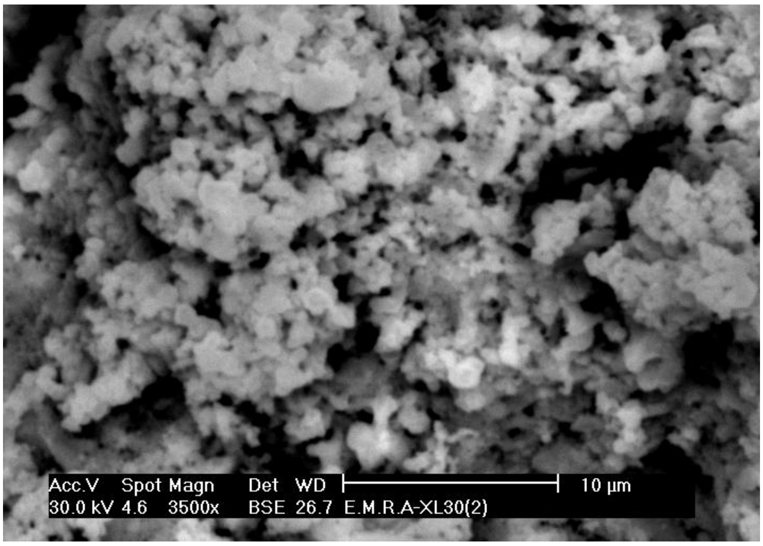

Fig. 13-c. SEM images of 10 wt. % CuO supported on washcoated cordierite calcined at 500 ^{o}C for 1hr soaking time at magnification 3500x.

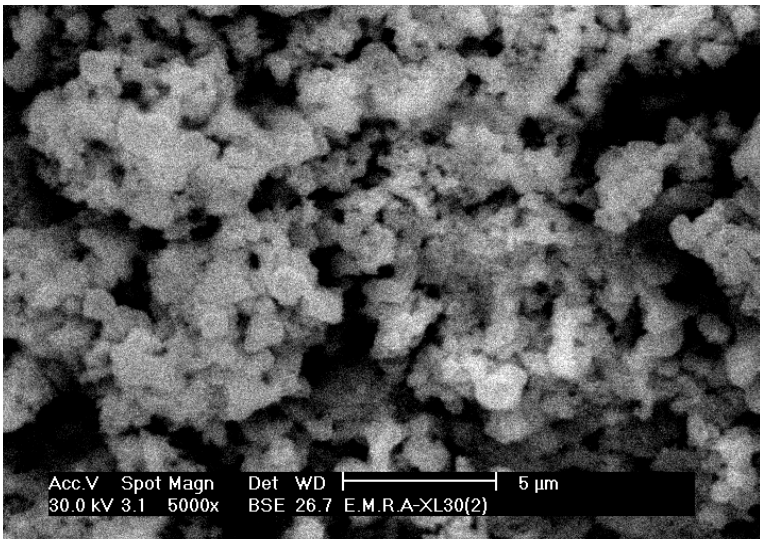

Fig. 13-d. SEM images of 10 wt. % CuO supported on washcoated cordierite calcined at 500 ^{o}C for 1hr soaking time at magnification 5000x.

Conclusion

In this work, nano Cu supported on washcoated cordierite was prepared by reduction method with hydrazine hydrate. Nano CuO supported on washcoated cordierite was prepared by calcination of the previously prepared Cu/washcoated cordierite at different temperatures. X-ray investigation showed that, the crystallite size of samples was in nano size. SEM showed that the dispersion of preheated Cu and CuO on washcoated cordierite was homogenous.

References

1. **Zhang, L.D. and Mu, J.M.,** *Nanoscale Materials and Nanostructures,* Science Press, Beijing (2001).

2. **El-Sayed, M.A**., Some interesting properties of metals confined in time and nanometer space of different shapes. *Acc. Chem. Res.* **34**, 257 (2001).

3. **Cao, Y.W., Jin R.C. and Mirkin, C.A.,** Nanoparticles with Raman spectroscopic fingerprints for DNA and RNA detection. *Science*, **297,** 1536 (2002).

4. **McFarland, A.D. and Van Duyne, R.P.,** Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity. *NanoLett.* **3,** 1057 (2003).

5. **Yu, A.M., Liang, Z.J., Cho, J.H. and Caruso, F.,** Nanostructured electrochemical sensor based on dense gold nanoparticle films., *NanoLett.* **3,** 1203 (2003).

6. **Savinova, E.R., Savinova, E.N. and Parmon, V.N.,** Copper colloids stabilized by water-soluble polymers. Part II. Their application as catalysts for dihydrogen evolution, *J. Mol. Catal.* **48**, 231. (1988).

7. **Narayanan, R. and El-Sayed, M.A.,** Effect of catalytic activity on the metallic nanoparticle size distribution: electron-transfer reaction between $Fe(CN)_6$ and thiosulfate ions catalyzed by PVP - platinum nanoparticles, *J. Phys. Chem.* **B 107**, 12416 (2003).

8. **Joshi, S.S., Patil, S.F., Iyer, V. and Mahumuni, S.** Radiation induced synthesis and characterization of copper nanoparticles, *Nanostruct. Mater*. **10**, 1135 (1998).

9. **Lisiecki, I. and Pileni, M.P.,** Synthesis of copper metallic clusters using reverse micelles as microreactors. *J. Am. Chem. Soc.* **115**, 3887 (1993).

10. **Pileni, M.P., Ninham, B.W., Gulik-Krzywicki, T., Tanori, J., Lisiecki, I. and Filankembo, A.,** Direct relationship between shape and size of template and synthesis of copper metal particles. *Adv. Mater.* **11**, 1358 (1999).

11. **Qi, L., Ma, J. and Shen, J.,** Synthesis of copper nanoparticles in nonionic water-in-oil microemulsions. *J. Colloid Interface Sci.* **186**, 498 (1997).

12. **Ziegler, K.J., Doty, R.C., Johnston, K.P. and Korgel, B.A.,** Synthesis of organic monolayer-stabilized copper nanocrystals in supercritical water. *J. Am. Chem. Soc.* **123**, 7797 (2001).

13. **Liu, Z. and Bando, Y.**, A novel method for preparing copper nanorods and nanowires. *Adv. Mater.* **15**, 303 (2003).

14. **Huang, H.H., Yan, F.Q., Kek, Y.M., Chew, C.H., Xu, G.Q., Ji, W., Oh, P.S. and Tang, S.H.,** Synthesis, characterization, and nonlinear optical properties of copper nanoparticles. *Langmuir*, **13**, 172 (1997).

15. **Lisiecki, I., Billoudet, F. and Pileni, M.P.,** Control of the shape and the size of copper metallic particles. *J. Phys. Chem.* **100**, 4160 (1996).

16. **Avgouropoulos, G. and Ioannides, T.,** Selective CO oxidation over CuO-CeO2 catalysts prepared via the urea–nitrate combustion method. *Appl. Catal.* **A 244,** 155–167 (2003).

17. **Avgouropoulos, G. and Ioannides, T.,** Adsorption and reaction of CO on CuO-CeO2 catalysts prepared by the combustion method. *Catal. Lett.* **116**, 15–22 (2007).

18. **Dong, L., Hu, Y., Shen, M., Jin, T. Wang, J., Ding, W. and Chen, Y.** Dispersion behaviors of copper oxide on the mixed "CeO_2 + γ-Al_2O_3" support. *Chem. Mater.* **13**, 4227–4232 (2001).

19. **Cao, J. L., Wang, Y., Zhang, T.Y., Wu, S.H. and Yuan, Z.Y.,** Preparation, characterization and catalytic behavior of nanostructured mesoporous $CuO/Ce_{0.8}Zr_{0.2}O_2$ catalysts for low-temperature CO oxidation. *Appl. Catal.* **B 78**, 120–128 (2008).

20. **Cao, J. L., Wang, Y., Yu, X.L., Wang, S.R., Wu, S.H. and Yuan, Z.Y.,** Mesoporous CuO-Fe_2O_3 composite catalysts for low-temperature carbon monoxide oxidation. *Appl. Catal.* **B 79**, 26–34 (2008).

21. **Fierro-Gonzalez, J.C. and Gates, B.C.,** Mononuclear Au^{III} and Au^{I} complexes bonded to zeolite NaY: Catalysts for CO oxidation at 298 K., *J. Phys. Chem.* **B 108** 16999–17002 (2004).

22. **Qu, Z., Giurgiu, L. and Roduner, E.**, ESR observation of the formation of an Au(II) complex in zeolite Y., *Chem. Commun.* **23**, pp. 2507–2509 (2006).

23. **Tu, C.H., Wang, A.Q., Zheng, M.Y., Wang, X.D. and Zhang, T.,** Factors influencing the catalytic activity of SBA-15-supported copper nanoparticles in CO oxidation. *Appl. Catal.* **A 297**, 40–47 (2006).

24. **Lian, H., Jia, M., Pan, W., Li, Y., Zhang, W. and Jiang, D.**, Gold-base catalysts supported on carbonate for low-temperature CO oxidation. *Catal. Commun.* **6,** 47-51 (2005).

25. **Ganesha, A.V., Basavalings, B., Tareen, J.A.K. and Pasha, M.A.**, Breakdown of synthetic potassic cordierite at low P-T conditions. *Curr. Sci.* **87**, 104–108 (2004).

26. **Kobayashi, Y., Sumi, K. and Kato, E.**, Preparation of dense cordierite ceramics from magnesium compounds and kaolinite without additives, *Ceram. Int.* **26**, 739–743 (2000).

27. **Tulyaganov, D.U., Tukhtaev, M.E., Escalante, J.I., Ribeiro, M.J. and Labrincha, J.A.**, Preparation of dense cordierite ceramics from magnesium compounds and kaolinite without additives., *J. Eur. Ceram. Soc.* **22**, 1775–1782 (2002).

28. **Kumar, S., Singh, K.K. and Ramachadrarao, P.**, Synthesis of cordierite from fly ash and its refractory properties., *J. Mater. Sci. Lett.* **19,** 1263–1265 (2000).

29. **Gonzalez-Velasco, J.R., Gutierrez-Ortiz, M.A. and Ferret, R.**, Synthesis of cordierite monolithic honeycomb by solid state reaction of precursor oxides. *J. Mater. Sci.* **34**, 1999–2002 (1999).

30. **Tamborenea, S., Mazzoni, A.D. and Aglietti, E.F.**, “Mechanochemical activation of minerals on the cordierite synthesis, *Thermochim. Acta* **411**, 224–219 (2003).

31. **Goodboy, K.P. and Downing, J.C.,** Production, processes, properties and applications for activated and catalytic aluminas. In: L.D. Hart Editor, *Alumina Chemicals : Science and Technology Handbook The American Ceramic Society Inc,* Westerville OH,USA, pp. 93-98 (1990).

32. **Blachou, V., Goula, D. and Philippopoulos, C.,** Wet milling of alumina and preparation of slurries for monolithic structures impregnation, *Ind. Eng. Chem. Res* **31**, 364–369 (1992).

33. **Scherrer, P.**, Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse p. 98, **2** (1918).

34. **Lee, J.D.,** *Concise Inorganic Chemistry*, 5th *ed.* Chapman and Hall, London (1996).

35. **Wli, C., Wang, H.R. Li, L.Q. and Qiun, Y.T.**, Preparation of nickel ultrafine powder and crystalline film by chemical control reduction., *Mater.Res.*, **10,** 2892 (1995).

36. **Li , Y.D., Li, L.Q., Liao, H.W. and Wang, H.R.,** Preparation of pure nickel, cobalt, nickel–cobalt and nickel–copper alloys by hydrothermal reduction. *J. Materials Chemistry*, **9**, 2675-2677 (1999).

(*Received* 17/8/2010 ;
accepted 14/9/2010)

تحضير وتوصيف حفازات النحاس واكاسيده المتناهية الصغر(النانو) المحملة على الكورديوريت المغطى

محمد محمد عبد المنعم سليم[أ] ، صلاح الدين عبده حسن[ب] ، محمد رمضان عبدالسلام رزق[ج] و نصر الله محمد دراز[أ، د]
[أ] قسم الكيمياء الفيزيقية – المركز القومى للبحوث ، [ب] قسم الكيمياء – كلية العلوم – جامعة عين شمس، [ج] وزارة البحث العلمى – القاهرة – مصر و [د] قسم الكيمياء – كلية العلوم - جامعة الملك سعود – السعودية .

تم تحضير فلز النحاس واكسيده المتناهى الصغر (النانو) محمل على الكورديوريت المغطى بالألومينا وذلك عن طريق الاختزال باستخدام الهيدرازين هيدريت في وسط غير مائى. تم دراسة تأثير درجات الحرارة على اكسيد النحاس عند ٥٠٠ ، ٦٠٠ و٧٠٠ درجة مئوية وتم توصيف العينات باستخدام تقنية حيود الأشعة السينية (XRD) ، ومجهر المسح الإلكتروني (SEM). واظهرت النتائج ان العينة المحتوية على ٥,٠ وزن ٪ من النحاس او الاكسيد المحمل على الكورديوريت المغطى بالالومينا والمسخن عند ٥٠٠ درجة مئوية لمدة ساعة له اقل حجم بلورى.