

Highly Dispersed CuO Nanoparticles on SBA-16 Type Mesoporous Silica with Cyclam SBA-16 as a Precursor

Eko Adi Prasetyanto, Sujandi, Seung-Cheol Lee, and Sang-Eon Park*

Laboratory of NanoGreen Catalysis and Nano Center for Fine Chemical Fusion Technology, Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: separk@inha.ac.kr
Received February 28, 2007

CuO nanoparticles were prepared onto SBA16 type mesoporous silica matrix using Cyclam complex, which was tethered into SBA16 mesopores for the accommodation of Cu cation as an intermediate. After removing this intermediate by calcination, CuO nanoparticles were generated inside SBA16 pore surfaces. The structural ordering and nanodispersion of CuO immobilized SBA16 were confirmed. The possible reason for the high structural ordering of CuOSBA16 might be the homogeneity of particle sizes and all the particles highly dispersed inside the SBA16 pore surfaces.

Key Words : SBA-16, CuO nanoparticles, Cyclam

Introduction

Mesoporous materials, such as M41s and SBA families, have been received great interest in catalysis because they possess uniformly large pore sizes (between 2.0 and 50.0 nm which are larger than microporous cavities (613 Å) of conventional zeolites) and high surface areas (up to 1200 m²/g).¹ Both pore sizes and surface areas make them to be excellent supports for new generation of heterogeneous catalysis and potential hosts for the inclusion of bulky organic and inorganic species. Among the reported cubic mesoporous silica materials, SBA16 appears to be one of the best candidates for catalytic support or absorbent applications because of the good thermal stability due to the thick wall, economical synthesis with inexpensive silica sources, and three dimensional cage structures.²⁻⁴

CuO supported catalysts can be pivotal candidates for heterogeneous catalysts, especially redox catalysts. For introducing metallic active sites to the silica support, several methods have been proposed: impregnation, ion exchanges, direct incorporation and grafting with organometallic compounds. And the catalytic activities of these particles generally depend on their sizes, shapes, and stabilizing agents, which are mainly dependent on the preparation conditions.^{5,6} In this sense, it is worth to investigate the synthesis methods and the properties of CuO particles in the support.

In this work, the copper cation was introduced onto pore of SBA16 using Cucyclam complex as precursor, followed calcined to be copper oxides. The cyclam has been a well known macrocyclic ligand that can accommodate and stabilize various transition metal cations having high oxidation state.^{7,8}

The structure and sorption properties of the obtained materials were studied by Xray diffraction (XRD), transmission electron microscopy (TEM), Near IR reflectance spectroscopy (NIR) and surface area measurements. The environment and accessibility of Copper were studied using electron paramagnetic resonance (EPR).

Experimental Procedure

Raw Materials. The surfactant F127 triblock copolymer (poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide)/EO106PO70EO106; MW12600; BASF), was used as the template. Sodium metasilicate (Na₂SiO₃·9H₂O; Sigma Aldrich) and 3-chloropropyl triethoxysilane/CPTS (Cl(CH₂)₃-Si(OEt)₃; Aldrich) were used as silica and chloropropyl group sources, respectively. CuCl₂·6H₂O and hydrochloric acid was purchased from Daejung Chemical Company. All the chemicals were used as received without further purification. The tetraazamacrocycle (cyclam) was synthesized according to the reported procedure.^{9,10}

Synthesis of SBA-16. Mesoporous silica SBA-16 type was synthesized according to following procedure; 16.0 g of 10% (w/w) aqueous solution of F127 was poured into 26.6 g distilled water followed by 4.36 g of sodium metasilicate (Na₂SiO₃·9H₂O) with vigorously stirring to get clear solution. Then, 13.0 g of concentrated hydrochloric acid (37.6%) was quickly added into the solution. The mixture was aged with stirring at 313 K for 1 hour. The obtained gel was subjected into microwave digestion system (CEM Corporation, MARS-5) under static conditions at 373 K for 2 hours and an operated power is 300 W (100%). To remove the template from the crystallize SBA-16, the powder was calcined in the oven at 773 K for 5 hours.

Synthesis of Cu-Cyclam-SBA-16 and CuO-SBA-16. Cu-Cyclam-SBA-16 was prepared by anchoring cyclam to mesoporous silica according to following procedure; A mixture of SBA-16 and Chloropropyl triethoxy silane in toluene was refluxed at 363 K with stirring for 8 hours. After filtration and drying, chloropropyl-SBA-16 was added by cyclam and was refluxed at 363 K in acetonitrile.

Characterization. The prepared samples were characterized by several instrumental analysis techniques. The crystallinity of the samples was measured using powder Xray powder diffraction (XRD) patterns which were obtained on a Rigaku diffractometer using CuK α radiation ($\lambda =$

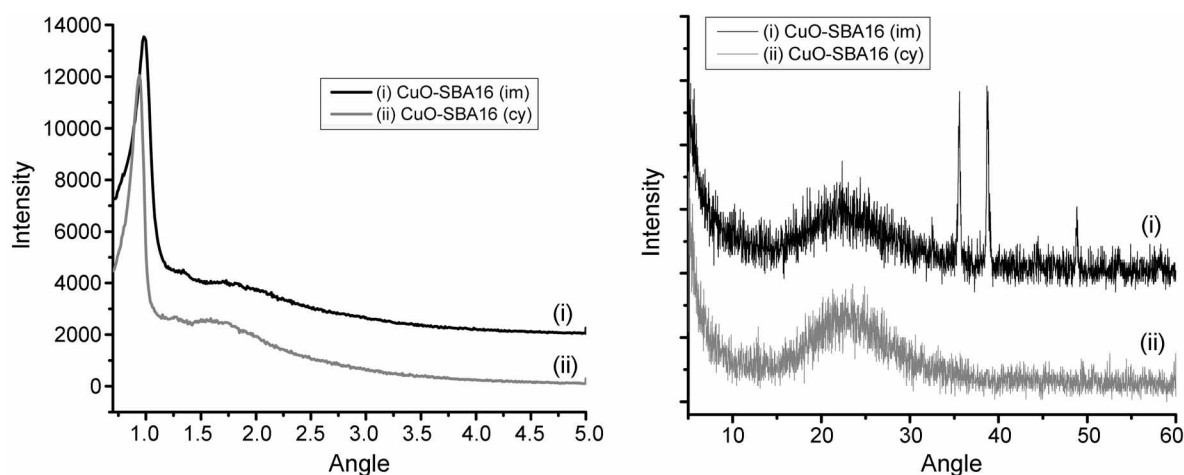


Figure 1. (a) Low angle XRD patterns of CuO-SBA-16 synthesized using Cu-Cyclam-SBA-16 as precursor and impregnation (b) Wide angle XRD patterns of CuO-SBA-16 synthesized using Cu-Cyclam-SBA-16 as precursor and impregnation.

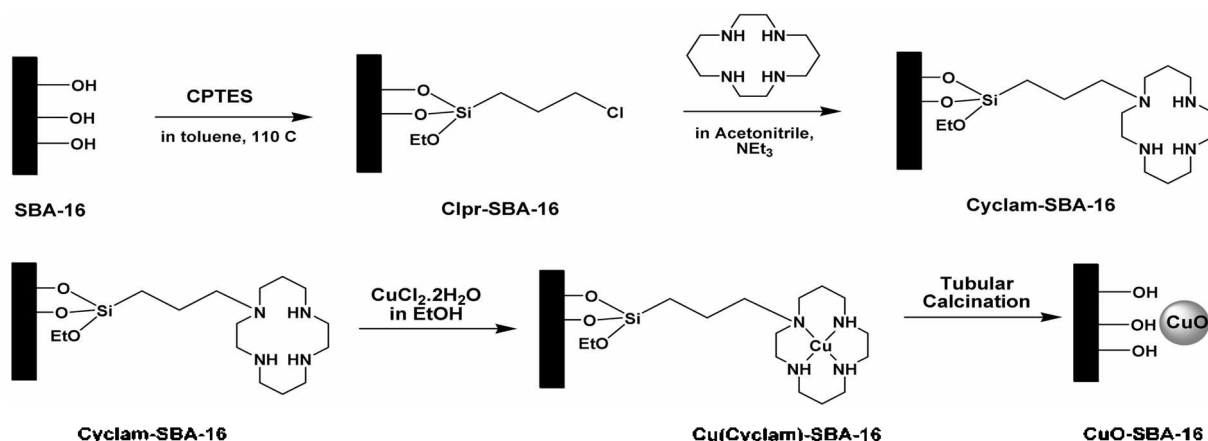
0.1547 nm). BET measurements including surface areas and pore volumes were performed using a Micromeritics porosimeter (model ASAP-2400). The samples were degassed at 300 °C for 3 h. The pore size distribution (PSD) was calculated using the Barrett-Joyner-Halenda (BJH) formula. UV-Vis-NIR diffuse reflectance spectra (DRUV) were measured with a Solidspec 3700 UV-Vis-NIR spectroscopy. The NIR spectra were recorded in the reflectance mode at room temperature. The EPR spectra were recorded with JEOL FA200 instrument.

Results and Discussion

Figure 1 shows the low angle XRD powder patterns of as-synthesized and calcined Cu-SBA-16, prepared *via* Cu-cyclam as precursor and impregnation methods. The patterns show typical characteristics of strong diffraction bands at low scattering angle 2θ , corresponding to d_{100} for the all samples. The Cu-cyclam-SBA-16 samples showed the decrease in the ordering peak comparing to that of the pure SBA-16 sample. After the Cu-Cyclam-SBA-16 sample was burned by tubular calciner to get CuO-SBA-16 nano-

particles, XRD pattern showed high diffraction and ordering peaks. In the other hand, the CuO-SBA-16 which was prepared by impregnation method also gives nice diffraction. At both methods, we draw out the conclusion that SBA-16 mesoporous silica could be really stable support for metal complex and metal oxide.

The UV-Vis-NIR spectra recorded in diffuse reflectance (DR) mode for the calcined copper (cyclam) anchored SBA-16 catalyst gave symmetric band at 757 nm due to d-d transitions of dispersed Cu^{2+} species ($3d^9$). The observed d-d transitions were in the range expected for Cu^{2+} species in an axially distorted octahedral (due to Jahn Teller Effect) environment of O-containing ligands. It should be noted that the presence of small but defined CuO particles would have given d-d transition shifted to lower wavelengths losing the asymmetric character from 870 nm of the bulk CuO transition. No evidence of absorption edges at 650 nm or at 890 nm, due to the energy gap of large particles of Cu_2O (Eg 15320 cm^{-1}) and of CuO (Eg 11290 cm^{-1}), respectively, was present in the spectra. At lower wavelength, DRS are dominated by strong absorption in 200-500 nm intervals, with maxima clearly distinguished at 226 nm and 250 nm



Scheme 1. Schematic illustration for the synthesis of CuO-SBA-16.

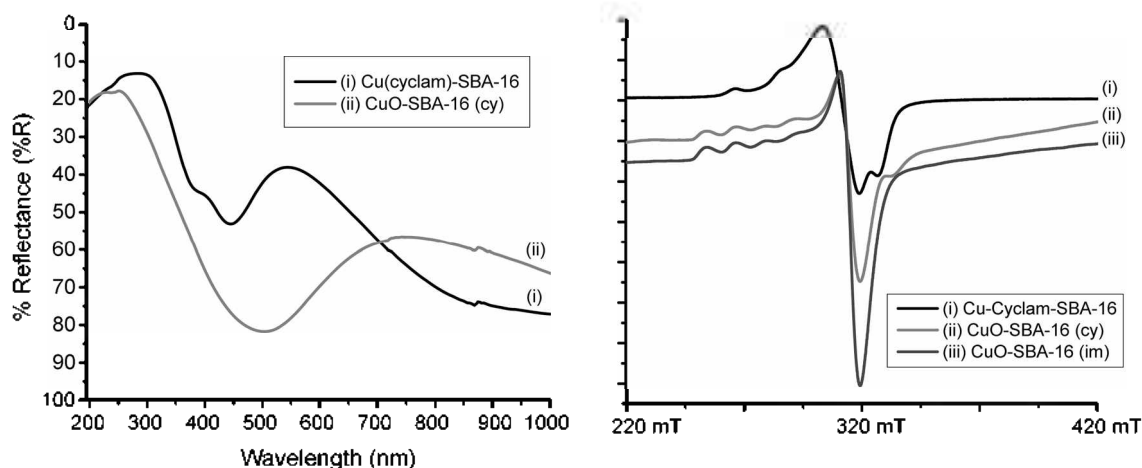


Figure 2. The UV-vis-NIR spectra recorded in diffuse reflectance (DRS) and EPR spectra of CuO-SBA-16 synthesized using Cu-Cyclam-SBA-16 as precursor and impregnation.

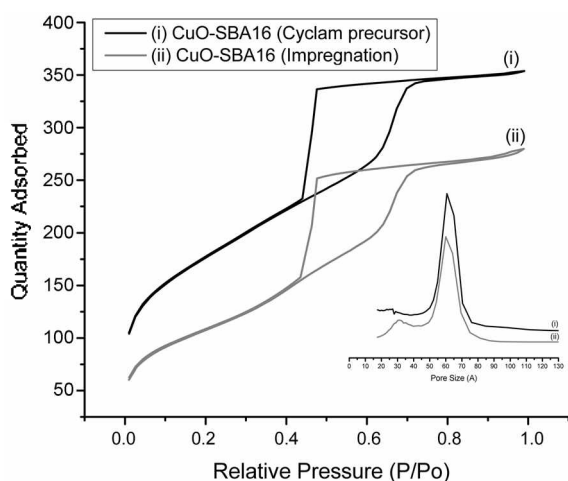


Figure 3. N_2 adsorption-desorption full isotherm and pore size distribution calculated by BJH method from desorption branch of CuO-SBA-16 (cy) and CuO-SBA-16 (im).

due to O^{2-} to Cu^{2+} charge-transfer transitions.

The copper oxide was formed during calcination of the assynthesized materials and supposed to be located in the cages of SBA-16. The results showed that the CuO particles were perfectly dispersed in the SBA-16 pore channels. Interestingly, the formations of larger particles were negligible. Differently from the case of CuO-SBA-16 which was prepared *via* Cu-Cyclam-SBA-16, CuO-SBA-16 prepared by impregnation method gave large particle size of CuO. It was proven by the appearance of the bands at 36, 39, and 49° of 2θ from wide angle XRD pattern. From the TEM images, we can observe the presence of large particle CuO (Figure 4). The particle size of CuO which generated by impregnation method are around 40 nm. In the other hand, large particle size generation of CuO can be avoided by Cu-Cyclam-SBA-16 as precursor method.

The nitrogen adsorption isotherms and BJH pore size distribution of the samples are shown in Figure 3. These isotherms had the "hysteresis loop" resembling the type IV isotherm, typical in mesoporous silica materials. BET

Table 1. Physical properties of CuO-SBA-16 (cy), and CuO-SBA-16 (im)

No	Sample	BET Surface Area	Pore Volume	Pore Size
1	CuO-SBA-16 (Cy)	618.9 m^2/g	0.54 cm^3/g	35.3 nm
2	CuO-SBA-16 (Im)	384.2 m^2/g	0.43 cm^3/g	45.0 nm

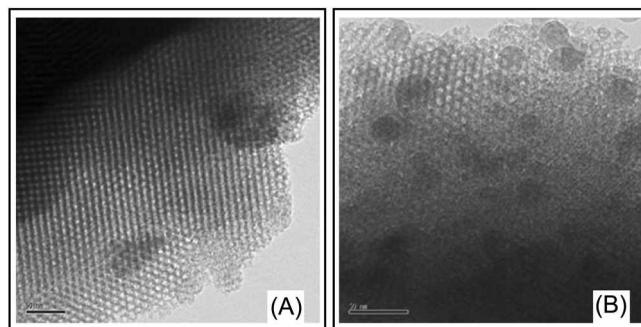


Figure 4. TEM image of CuO-SBA-16 synthesized using Cu-Cyclam-SBA-16 as precursor (A) and impregnation (B).

surface areas measured from these isotherms were 618 and 384 m^2/g for CuO-SBA-16 (cy) and CuO-SBA-16 (im), respectively and the pore volume were 0.547 and 0.432 cm^3/g (Table 1). The decrease of surface area caused by the presence of large size of CuO which prepared by impregnation method. Preparation by Cu-Cyclam complex grafting method could maintain the small particle size of CuO. The larger pore volume was indicating this. The average pore size of sample was prepared by cyclam complex, calculated by BJH method, was similar with the sample prepared by impregnation. This was indicating the nature of SBA16 could be maintained.

To figure out the electronic properties of CuO in each sample, we examined CuO-SBA-16 (cy) and CuO-SBA-16 (im) samples by EPR. Electron Paramagnetic Resonance (EPR) is a sensitive spectroscopic method for the determination of the geometric and electronic structure, the dynamics and the spatial distribution of paramagnetic species in

materials. Figure 2 shows the EPR spectra of CuO-SBA-16 (cy) and CuO-SBA-16 (im), respectively. The spectra of CuO-SBA-16 (cy) was recorded at 300, 280 and 220 K and CuO-SBA-16 (im) samples was recorded at 280 and 220 K. The spectrum of the CuO-SBA-16 (cy) could be described by an axial spin Hamiltonian with parameters $g_{\parallel} = 2.29$, $g_{\perp} = 2.13$ and $A_{\parallel} = 0.0168 \text{ cm}^{-1}$ which point to a square planar symmetry for Cu(II) ions coordinated to four nitrogens. The EPR intensity of CuO-SBA-16 (im) sample was much higher in comparison with the CuO-SBA-16 (cy) sample. Since all spectra were measured under the same conditions, we can conclude that the concentration of Cu(II) ions in the CuO-SBA-16 (im) higher than CuO-SBA-16 (cy) sample, respectively.

Conclusions

Highly dispersed CuO onto SBA-16 type mesoporous silica was successively prepared by introducing cyclam as a host for copper cation after tethering chloropropyl group onto the pore of SBA-16 matrix followed by tubular calcinations for the as-synthesized materials at 833 K for 7 h. CuO particles seemed to be accommodated uniformly in the internal pore of SBA-16 support. These CuO particles were highly dispersed and not agglomerated.

Acknowledgement. Authors are gratefully acknowledging the support by Defense Acquisition Program Administration and Agency for Defense Development.

References

1. Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
2. Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
3. Sakamoto, Y.; Kaneda, M.; Terasaki, O.; Zhao, D.; Kim, J. M.; Stucky, G. D.; Shin, H. Y.; Ryoo, R. *Nature* **2000**, *408*, 449.
4. Hwang, Y. K.; Chang, J.-S.; Kwon, Y.-U.; Park, S.-E. *Micropor. Mesopor. Mater.* **2004**, *68*, 21.
5. Bonnemant, H.; Brijoux, W.; Brinkmann, R.; Fretzen, R.; Jousen, T.; Koppler, R.; Korall, B.; Neiteler, P.; Richter, J. *J. Mol. Catal.* **1994**, *86*.
6. Luo, W.; Wang, G.; Wang, J. *Ind. Eng. Chem. Res.* **2006**, *45*(1), 129.
7. Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, 1989.
8. Harrowfield, J. M.; Kim, Y.; Koutsantonis, G. A.; Lee, Y. H.; Thuéry, P. *Inorg. Chem.* **2004**, *43*, 1689.
9. Barefield, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R. In *Inorganic Synthesis*; Basolo, F., Ed.; McGraw-Hill: New York, 1976; Vol. 16, p 220.
10. Sujandi; Han, S. C.; Han, D.-S.; Jin, M.-J.; Park, S.-E. *J. Catal.* **2006**, *243*, 150.