



Synthesis and Characterization of Novel Mesoporous CuO and Its Application to CO₂ Capture

MEI MEI PENG, PUSHPARAJ HEMALATHA, MANI GANESH, RAJANGAM VINODH and HYUN TAE JANG*

Department of Chemical Engineering, Hanseo University, 360 Daegok-ri, Haemi-myun, Seosan-si 356 706, Chungcheongnam-do, South Korea

*Corresponding author: Tel : + 82 41 6601423; E-mail: htjang@hanseo.ac.kr

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A new mesoporous CuO nanoparticles has been synthesized successfully by using mesoporous carbon as template and cupric nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) as copper source. The synthesized meso porous CuO was characterized with XRD, TGA, SEM and BET. The result revealed that the synthesized porous CuO has high mesoporous surface area and crystal structure with uniform sized spherical crystal particles. The specific surface area (S_{BET}) of synthesized CuO was found to be $153.46 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume (V_p) of $0.1516 \text{ cm}^3 \text{ g}^{-1}$ and average pore size of 3.9 nm, which was much higher than that of commercial CuO (S_{BET} , $7.6 \text{ m}^2 \text{ g}^{-1}$; V_p , $0.01 \text{ cm}^3 \text{ g}^{-1}$). The CO₂ studies also revealed that the synthesized CuO nanoparticles have maximum CO₂ adsorption of about 75 mg/g (7.5 wt %) at room temperature and pressure.

Key Words: Mesoporous carbon, porous CuO, CO₂ capture.

INTRODUCTION

Carbon dioxide emission and global warming were found to inter related to each other. While compared to the other global warming gases CO₂ is found to be the most lethal one. High accumulation of CO₂ into atmosphere is mainly caused by the continuous utilization coal by power plants for energy. World energy requirements mainly depend on coal, hence its utilization can't be controllable. The only way to minimize the fast accumulation into air by find a way for its effective removal using physical sorbents, due to their ease in regeneration and less energy requirement for the same will make them more ideal than liquid amine sorbents works on chemisorptions. Among the physical sorbents porous material have vast application in gas sorption. Meso silica¹⁻³, amine functionalized silica⁴⁻⁶, metal oxide functionalized meso silica⁷ and zeolites⁸⁻¹¹ were studied extensively to accomplishing this goal. Most recently metal organic frameworks¹²⁻¹⁷, covalent organic framework¹⁸⁻²¹, elemental organic framework and covalent organic polymers²²⁻²⁴ were also developed and studied for CO₂ adsorption. Until now none of the above listed material found their commercial opportunity to the specific task due to their lack in selectivity or cost of production. Yet now alkaline and transition metal oxides are also found as an attractive material for CO₂ adsorption at high temperature. Among them porous metal oxide have the capacity to adsorb CO₂ even at low temperature.

In this regards, metal oxides were synthesized by various route such as sol gel, coprecipitation in presence of surfactants

and hard templating route. Huwe and Froba²⁵ synthesized iron, copper, nickel, cobalt, manganese and zinc in the form of oxides inside the mesoporous carbon CMK-3 by a wet impregnation. Hu *et al.*²⁶ reported a recyclable catalyst-sorbent Fe/CMK-3 and studied its adsorption performance of phenol. In case of using hard templates mesosilica or meso carbon is one of the attractive routes to synthesis mesoporous metal oxides. In our present report, we also attempted to synthesize mesoporous CuO using meso carbon as template and testing the synthesized CuO for its CO₂ adsorption capability.

EXPERIMENTAL

Synthesis of silica template SBA-15: SBA-15 was synthesized using pluronic P123 as a structural directing template. In a typical synthesis 0.8 g P123 was dissolved in a mixture of 20 g H₂O and 6 g 37 % HCl under vigorous stirring. 6.125 g TEOS was added to the mixture solution drop by drop. The synthesis mixture was stirred for 24 h at 35-40 °C, then the container was sealed and kept at 100 °C for 24 h to aid solvothermal conditions. The mixture with silica precipitate was get down to room temperature by natural cooling then filtered and washed with copious amount of deionized water and ethanol to remove the excess of template prior to calcination. After dried at 40-50 °C oven overnight, the solid product was calcinated at 200 °C for 3 h and subsequently 500 °C for 4 h at a rate of 1 °C/min in air atmosphere.

Synthesis of mesoporous carbon CMK-3: The procedure given by Jun²⁷ was adapted to synthesize CMK-3. In a

typical synthesis, 2.5 g sucrose was dissolved in solution contains 0.28 g H₂SO₄ in 10 mL H₂O, then 2 g of SBA-15 sample was added to this solution and mixed homogeneously. The obtained paste was heated in an oven at 100 °C for 6 h followed by 160 °C for 6 h. This yielded a black powder, which was then again mixed with a solution contains 1.6 g sucrose in 10 mL solution contains 0.18 g H₂SO₄ in 10 ml H₂O. The prepared paste was reheated with a same heating program, used before. Obtained black powder was then carbonized at 900 °C for 6 h with a ramp of 1 °C/min in N₂ atmosphere. From carbonized sample the silica template was removed by treating it with 15 % HF followed by repeated washing with distilled water, until a neutral pH is reached. The obtained carbon (CMK-3) was then dried at 100 °C and stored in a desiccator²⁸.

Synthesis of porous CuO: The CuO incorporated mesoporous carbon CMK-3 was harvested from the wet impregnation method as reported by the Huwe and Froba²⁹. The typical synthesis was as follows: 19.32 g Cu(NO₃)₂ was dissolved in 50 mL ethanol to obtain 1.6 M metal nitrate solution, 0.5 g CMK-3 was added to the above solution and stirred for 24 h at room temperature. Then the solid was separated from the solution by centrifugation at a rate of 2900 rpm for 5 min (FLETA 5, Hanil Science Industries, Korea). The resulting material was dried in vacuum at room temperature. Then the sample was heated to 300 °C in an air stream for 6 h for the transformation from the nitrate to the oxide form²⁵.

Characterization: Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2200 + Ultima diffractometer with Cu-K α radiation ($\lambda = 0.154$ nm). The diffraction data were recorded in the 2 θ range 10–80° at step of 0.02 °/s. Thermogravimetric analysis (TGA) was performed using SCINCO thermal gravimeter N-1000, the sample was heated from room temperature to 800 °C under N₂ at a heating rate of 5 °C/min. The nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 200 °C under vacuum ($p < 10^{-5}$ mbar) for 6 hours in the degas port. The specific surface area, S_{BET} was determined from the linear part of the BET equation and the pore volume was calculated using a BET plot based on the amount of nitrogen gas adsorbed at the last adsorption point ($P/P_0 = 0.98$) and the pore size distribution using the Barrett-Joyner-Halenda (BJH) method. SEM images were captured on JEOL JSM 5600 scanning electron microscope.

CO₂ adsorption: CO₂ adsorption-desorption measurements for porous CuO were performed using Thermogravimetric Analyzer. A sample weight of approximately 10 mg was loaded into an alumina sample pan in a TG unit (SCINCO thermal gravimeter N-1000) and tested for CO₂ adsorption-desorption performance. The initial activation of the samples was carried out at 200 °C for 1 h in a nitrogen atmosphere. Then adsorption run was conducted using high purity CO₂ (99.99 %) gas and the desorption run was conducted in N₂ flow. The adsorption runs were conducted at 25, 50 and 75 °C under atmospheric conditions and desorption was determined at 200 °C. Both the gases, CO₂ and N₂ were passed through an

automatic valve, assisted with a timer for continuous adsorption and desorption profiles.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of CMK-3, porous CuO and commercial CuO. Two sharp crystal peaks appear at high 2 θ values of 35.4 and 38.6° represent the peak for CuO, it displays that the porous CuO sample obtained from calcination of Cu-CMK-3 sample at 300°C has a high purity of CuO crystal.

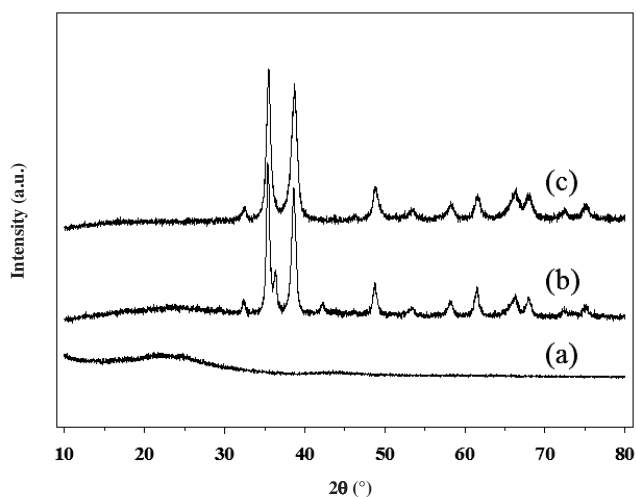


Fig. 1. XRD patterns of CMK-3, porous CuO and commercial CuO.

The thermal stability of the porous CuO sample as analyzed by TGA is presented in Fig. 2. The TGA results show that there are two weight losses from 100 to 400 °C. The first weight loss of about 6 % is due to loss of moisture content and physisorbed CO₂ on exposure to atmosphere. The second weight loss around 400 °C is due to the decomposition of the support mesoporous carbon CMK-3.

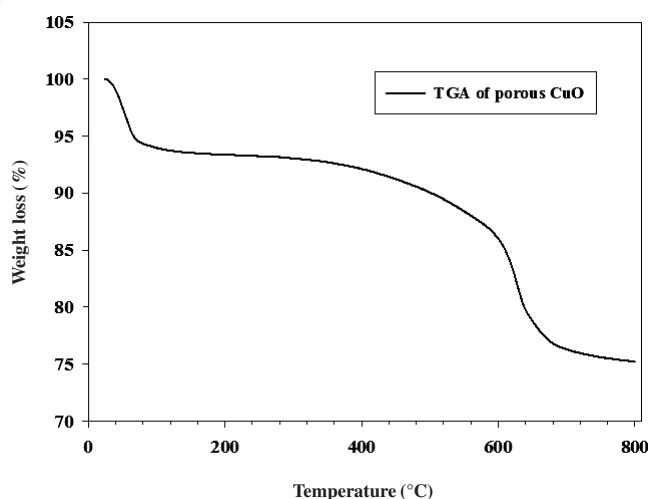


Fig. 2. TGA curve of porous CuO sample.

The N₂ adsorption/desorption isotherms of CMK-3, Cu-CMK-3 and porous CuO displayed type IV isotherms (Figs. 3 and 4), a signature characteristic of mesoporous materials. The surface area was decreased from CMK-3 to Cu-CMK-3 as

shown in Table-1, it reveals Cu was successfully doped to mesoporous carbon CMK-3. After calcination at 300 °C, the surface area the CuO sample was found to be 153.46 m² g⁻¹ with a total pore volume (V_p) of 0.1516 cm³ g⁻¹ and the pore size was calculated to be 3.9 nm.

Sample	S _{BET} (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
CMK-3	1053.5	1.1962	4.5417
Cu-CMK-3	358.52	0.2996	3.3426
Porous CuO	153.46	0.1516	3.9528

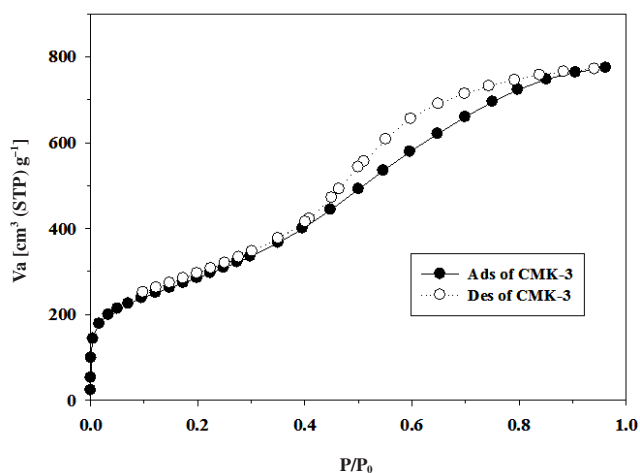


Fig.3. Nitrogen adsorption/desorption isotherm of CMK-3

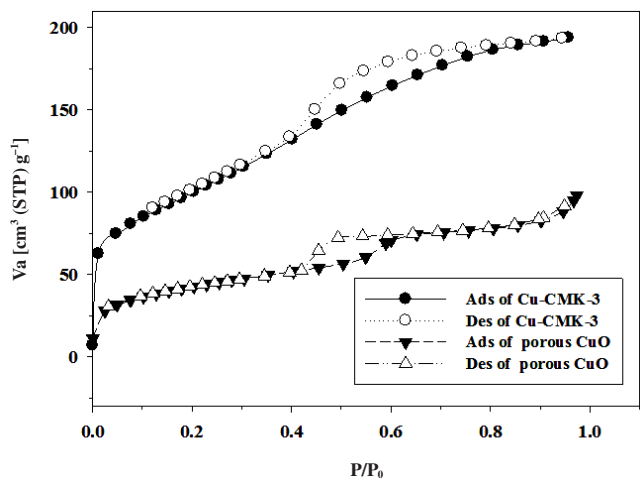


Fig. 4. Nitrogen adsorption/desorption isotherms of Cu-CMK-3 and porous CuO

The SEM image of the porous CuO sample after calcinations at 300 °C is presented in Fig. 5. The obtained CuO sample was resulted with agglomerated spherical particles.

CO₂ adsorption: Fig. 6 shows CO₂ adsorption/desorption profiles of porous CuO sample carried out at 25, 50 and 75 °C under the pressure of 1 bar. The CO₂ adsorption/desorption profiles illustrates the initial weight loss of approximately 3.75 wt % after preliminary activation at 200 °C in N₂ atmosphere is due to loss of moisture content and physisorbed

CO₂ on exposure to atmosphere. The maximum CO₂ adsorption capacity of CuO sample is 75.0 mg/g of the sorbent (1.70 mol/kg) at 25 °C.

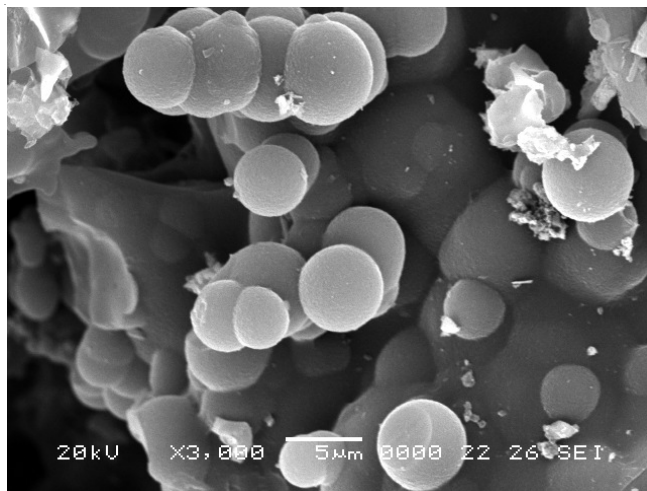


Fig. 5. SEM image of porous CuO

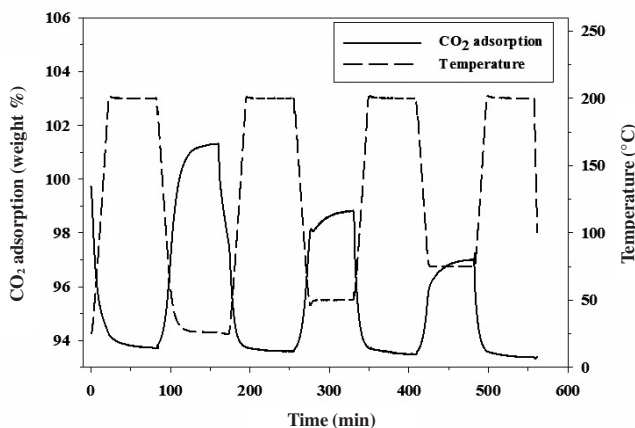


Fig.6. CO₂ adsorption/desorption profiles of porous CuO

The repeatability of porous CuO was verified by carrying four consecutive CO₂ adsorption-desorption runs at 25 °C (adsorption) and 200 °C (desorption) with pure CO₂ (99.99 %) feed gas. No apparent change in CO₂ uptake was observed as shown in Fig. 7. This result suggests that the porous CuO synthesized in this work is reusable.

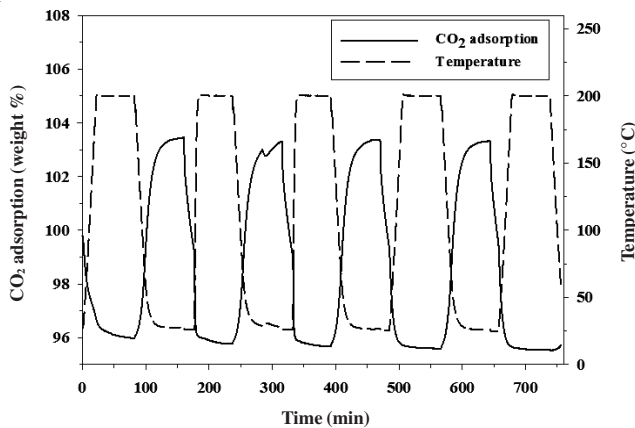


Fig.7. Recyclability of CO₂ adsorption at 25 °C of porous CuO

Conclusions

Mesoporous CuO was successfully synthesized through a hard templating method using mesoporous carbon as template. The results revealed that the obtained CuO sample was highly porous with high surface area and phase purity. The thermal stability of the CuO sample was investigated by TGA curve, which displayed that the CuO sample was thermally stable up to 400 °C. The materials synthe-sized here show a CO₂ adsorption capacity of about 75.0 mg/g (7.5 wt %) of the sorbent at 25 °C and about 7 wt % at 50 °C. The CO₂ adsorption study further revealed that the material is completely regenerable at 200 °C. The results proved that the material has high potential to adsorb CO₂ from the atmosphere and completely regenerable. From this, it is concluded that the porous CuO synthesized here is one of the material choice for low temperature CO₂ adsorption.

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