Synthesis of mesoporous carbon supported CuO: a new sorbent for CO_2 Caapture

Dae Kyung Kim, Mei Mei Peng, Joo Bo Lee, Ui Min Jeong,
Kyung Ran Back, Sung Hwa Song, Abidov Aziz, Hyun Tae Jang*
Chemical Engineering Department, Hanseo University
e-mail:htjang@hanseo.ac.kr

이산화탄소 포집용 CuO담지 메조포러스 탄소체 합성

김대경, 팽메이메이, 이주보, 정의민, 백경란, 송성화, 아비도브아지즈, 장현태
한서대학교 화학공학과

Abstract

In this study we synthesized mesoporous carbon supported CuO by using mesoporous silica i.e. SBA-15 as the template and cupric nitrate trihydrate ($Cu(NO_3)_2 3H_2O$)as copper source. The porous CuO was characterized with XRD, TGA, SEM and BET. The result reveals porous CuO has good crystal structure with uniform size of spherical crystal particles. The surface are a (S_{BET}) of porous CuO was found to be $153.46 m^2 g^{-1}$ with a total pore volume (V_p)of0.1516 $cm^3 g^{-1}$ and average pore size of 3.9 nm which was much higher than that of commercial CuO (S_{BET}, 7.6 $m^2 g^{-1}$; V_p, $0.01 cm^3 g^{-1}$). The obtained porous CuO was studied for adsorption of $CO_2$and the maximum CO_2 adsorption capacity was found to be 67.5 mg/g of the sorbent at 25 °C.

Keywords : Mesoporous carbon, Cu-CMK, porous CuO, CO_2capture.

1. Introduction

Mesoporous carbon molecular sieves first reported by Ryoo and coworkers [1] has drawn much attention in many fields such as catalyst supports for fuel cell, carbon electrode for supercapacitor, chromatography separation, adsorption to large molecules and desulfurization for clean energy because of their properties, like uniform pore size distribution, large specific surface area, tunable porosity, well-defined surface and so on. These materials (CMK-n, n=1~9) have been synthesized using well-ordered hexagonal and cubic mesoporous silica or alumino silicate materials as inorganic templates. An ordered mesoporous carbon named as CMK-3, which was synthesized by using highly ordered mesoporous silica SBA-15 as the template and sucrose as the carbon precursor, has an extremely high surface area, a large pore volume, chemical inertness, excellent mechanical stability, good thermal stability and electrical conductivity, and has been widely used in catalyst supports, absorbents, hydrogen storage media and advanced electrodes. In addition, CMK-3 can also be used as host materials to generate composites systems with special properties, such as synthesis of transition metal oxides inside the pore system of mesoporous carbon CMK-3. Li et al reported a series of ordered mesoporous nickel oxide/carbon (NiO/C) nanocomposites by a combination of "nanocasting" and thermolysis and studied its characteristics [2]. Huwe et al synthesized iron, copper, nickel, cobalt, manganese and zinc in the form of oxides inside the mesoporous carbon CMK-3 by a wet impregnation, drying and calcination procedure [3]. Recently, Hu et al reported a recyclable catalyst-sorbent Fe/CMK-3 and studied its adsorption performance of phenol [4]. In this study we synthesized porous CuO using mesoporous CMK-3 as host material and cupric nitrate trihydrate ($Cu(NO_3)_2 3H_2O$) as copper source. The porous CuO was characterized with XRD, TGA, SEM and BET. Finally, we studied its adsorption performance of CO_2, which was the first time to report the application of copper oxide incorporated mesoporous carbon in CO_2 gas adsorption.

2. Experimental

2.1. Synthesis of silica template SBA-15
SBA-15 was synthesized using pluronic P123 as a

templating agent. 0.8 g P123 was dissolved in a mixture of 20 g H_2O and6g37% HCl under vigorous stirring. 6.125g TEOS was added to the mixture solution drop by drop. The synthesis mixture was stirred for 24 h at 35~40 °C, then sealed and kept the mixture at 100 °C for 24 h, followed by cooling to room temperature, filtering and washing with 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 3h and subsequently 500 °C for 4 h at a rate of 1 °C/min in air atmosphere.

2.2. Synthesis of mesoporous carbon CMK−3

The preparation of CMK-3 was referred from a work of Jun et al. [5]. In a typical synthesis, 2.5 g sucrose was dissolved in 10 ml H_2SO_4 solution which contains 0.28g H_2SO_4 in 10ml H_2O, 2.0g 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 and subsequently at 160 ∘C for 6 h. This yielded a black powder, which was then again mixed with sucrose solution of 1.6 g sucrose and 10 ml H_2SO_4 solution which contains 0.18g H_2SO_4 in 10ml H_2O. The prepared paste was reheated with a same heating program, used before. Obtained black powder was then heating at 900 ∘C for 6 h with a ramp of 1 ∘C/min in N_2 atmosphere. From carbonized samples the silica template was removed by treating it with 15% HF acid 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 dessicator [6].

2.3. Synthesis of mesoporous carbon supported CuO

The CuO incorporated mesoporous carbon CMK-3 was harvested from the wet impregnation method as reported by the authors [7]. 19.32 g $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 50ml ethanol to obtain 1.6mol are thanolic metal nitrate solution, 0.5 g CMK-3 was added to the solution and stirred for 24 h at room temperature. The carbon‐metal nitrate composition was separated from the solution by centrifugation at a rate of 2900 rotations/min for 5 min. The resulting material was dried in vacuum at room temperature. Then the sample was heating to 300 °C in an air stream for 6 h the transformation from the nitrate to the oxide form was achieved [8].

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Miniflex diffractometer with Cu-Kα radiation (λ=0.154 nm).). The diffraction data were recorded in the 2Ɵ range 10-80 ° at step of 0.02 °/s. Thermogravimetric analysis (TGA) was performed by means of a SCINCO thermal gravimeter N-1000, the sample was heated from room temperature to 800 °C under N_2 at as can 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 6hours in the degas port. The specific surface area, S_{BET} was determined from the line arpart 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 JEOLJSM 5600 scanning electron microscope.
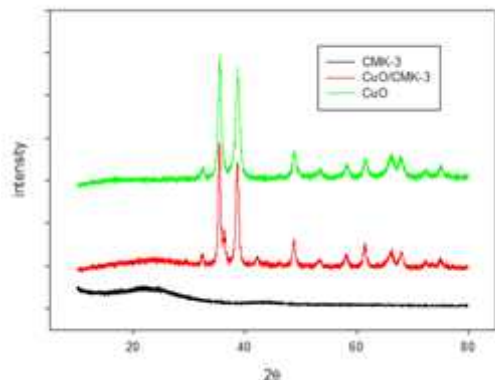
2.5. CO_2 adsorption

CO_2 adsorption‐desorption measurements for porous CuO were performed using Thermo Gravimetric 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 CO_2 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 CO_2(99.999%) gas, and the desorption run was conducted in N_2 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, CO_2 and N_2 were passed through an automatic valve, assisted with a timer for continuous adsorption and desorption profiles.

3. Results and Discussions

3.1. XRD analysis

Fig. 1 shows the XRD patterns of CMK-3, porous CuO and commercial CuO. Two sharp crystal peaks

appear at high 2θ values of 35.4° and 38.6°, which were the feature peaks of 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.

After calcination at 300°C, the surface area the CuO sample was found to be 153.46 m^2g^{-1} with a total pore volume (V_p) of 0.1516 cm^3g^{-1}, and the pore size was calculated to be 3.9 nm.

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

3.2. TGA analysis

The thermal stability of the porous CuO sample as analyzed by TGA is presented in Fig.2. The TGA results show that there is a weight loss from 100 °C to 400 °C. The first weight loss of about 6% is due to loss of moisture content and physisorbed CO_2 on exposure to atmosphere. The second weight loss around 400°C is due to the decomposition of the support mesoporo carbon CMK-3
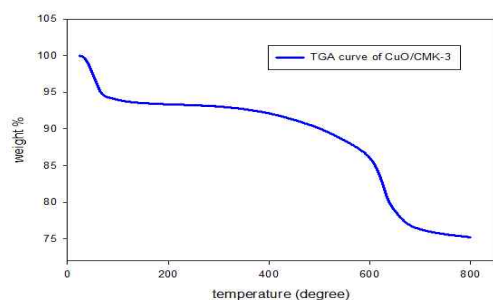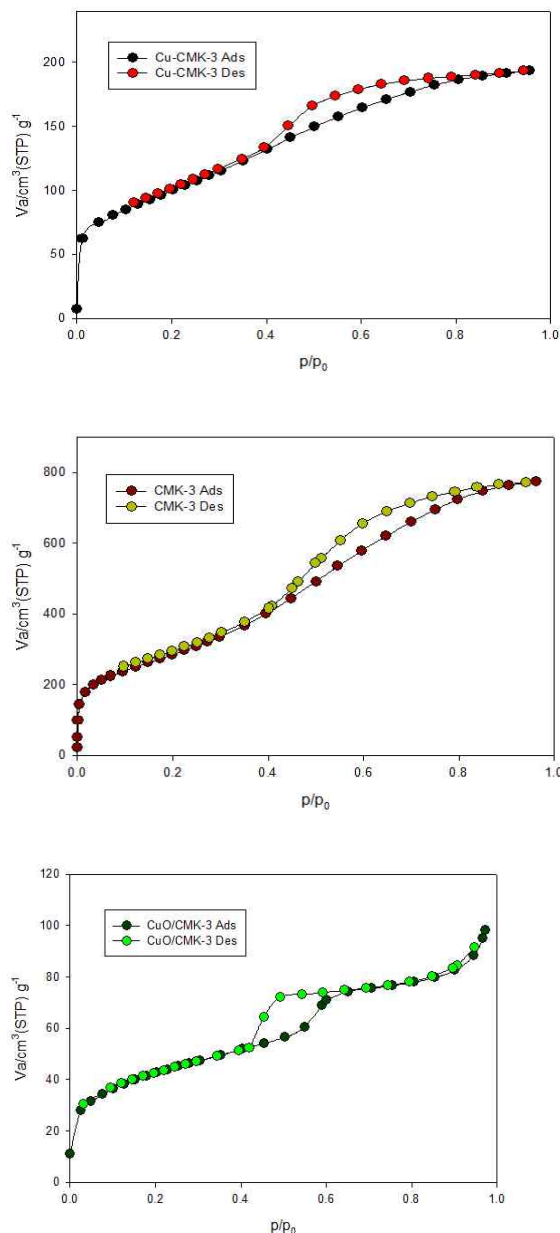

[Fig. 2] TGA curve of porous CuO sample.

3.3. BET analysis

The N₂ adsorption/desorption is otherms of CMK-3, Cu-CMK-3 and porous CuO displayed

type IV isotherms (as show in Fig.3), 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.


[Fig.3] nitrogen adsorption/desorption isothermals of CMK-3, Cu-CMK-3 and porous CuO.

[Table 1] BET data of CMK-3, Cu-CMK-3 and porous CuO.

| name	a/BET (m^2g^{-1})	Total pore volume (cm^3g^{-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

3.4. SEM analysis

The SEM image of the porous CuO sample after calcination at 300°C is presented in Fig. 4. The obtained CuO sample was composed by spherical particles with a particle size of 5×10^3 nm.
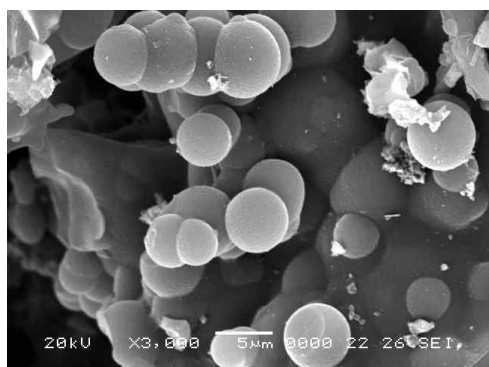
[Fig.4] SEM images of porous CuO.

3.5. CO_2 adsorption

Fig. 5 shows CO_2 adsorption/desorption profiles of porous CuO sample carried out at 25, 50 and 75 °C under the pressure of 1 bar. The CO_2 adsorption/desorption profile sill ustrates the initial weight loss of approximately 3.75wt% after preliminary activation at 200°C in N_2 atmosphere is due to loss of moisture content and physisorbed CO_2 on exposure to atmosphere. The maximum CO_2 adsorption capacity of CuO sample is 67.5 mg/g of the sorbent (1.53 mol/kg) at 25 °C.
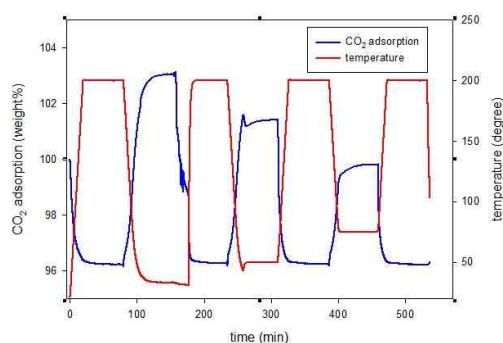
[Fig.5] CO_2 adsorption/desorption profiles of porous CuO.

4. Conclusions

Order mseoporous carbon supported CuO was successfully synthesized from a wet impregnation method. The result product was characterized with XRD, TGA, SEM and BET analysis. XRD and SEM results reveal the obtained CuO sample has high purity of crystal structure. The thermal thermal stability of the CuO sample was investigated by TGA curve, which displayed that the CuO sample was thermal stable until 400°C. The Nitrogen adsorption-desorption of porous CuO displayed type IV isotherms. The BET surface area (S_{BET}) was found to be $153.46 m^2 g^{-1}$ with a total pore volume (V_p) of 0.1516 $cm^3 g^{-1}$ and average pore size of 3.9 nm. The maximum CO_2 adsorption capacity was found to be 67.5 mg/g of the sorbent at 25 °C, and the porous CuO was found to regenerable and recyclable.

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