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ScienceDirect
Procedia Engineering 148 (2016) 30 – 34
Procedia Engineering
www.elsevier.com/locate/procedia

4th International Conference on Process Engineering and Advanced Materials

Crystal Growth of Cyclodextrin-based Metal-Organic Framework for Carbon Dioxide Capture and Separation

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Abstract

Crystalline cyclodextrin-based metal-organic framework (CD-MOF) was synthesized by vapor diffusion of methanol into a KOH solution of ɤ-cyclodextrin (ɤ-CD). Its CO_2 adsorption behaviors were evaluated both qualitatively and quantitatively. The adsorption behaviors of CD-MOF to separate and capture CO_2 have been tested by using thermogravimetric analysis in the multiple adsorption-desorption process. The chemical sorption of CO_2 was found to be caused by the formation of reversible carbonic acid. The adsorption amount of CO_2 was tested in pure CO_2 gas and 25vol% CO_2 in Ar gas. As a result, there is no difference of the adsorption amount against the CO_2 concentration and the saturated adsorption amount was 24 mg-CO_2/g-CD-MOF at 30°C.

Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords: CD-MOF; CO_2 adsorption; cyclodextrin

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Peer-review under responsibility of the organizing committee of ICPEAM 2016
doi:10.1016/j.proeng.2016.06.480

1. Introduction

To achieve the 2°C target from a global agreement (COP21) on climate change, it is crucial to mitigate anthropogenic CO_2 emissions, and especially reduce CO_2 emission from the power sector by 2030s. Hence, Carbon Capture and Sequestration (CCS) plays a vital role in reducing CO_2 emissions while satisfying fossil fuels demand by allowing low-carbon electricity generation with an acceptable carbon footprint. It consists of three major components which are CO_2 capture, transportation and storage. For the capture and separation of CO_2, there are several techniques available such as absorption, membrane separation, cryogenic distillation, biological methods, and adsorption. However, adsorption is the most common method to capture CO_2 because of its high adsorption capacity, low cost, low energy requirements and easy to operate. Although various adsorbents such as activated carbon and zeolite have been studied extensively, there are many issues to realize commercial CO_2 plant. The main shortcoming of activated carbon is the limitation of CO_2 adsorption condition at high pressure and has low selectivity [1,2] while hydrophilic zeolite is not stable in the presence of water [3]. Solid adsorbents operating at low temperature are beneficial for the effective utilization of energy in CCS plants due to the slight temperature difference from flue gas.

A new class of highly porous crystalline materials, metal-organic frameworks (MOFs) which possess controllable pore structures and tunable pore structure properties has emerged as a solution for carbon capture [4,5] but the major drawback for MOFs is that the organic precursors are high cost, non-renewable and harmful. Recently, CD-MOF has been designed from renewable ɤ-cyclodextrin (ɤ-CD) [6,7]. A single cubic unit of CD-MOF, $(\gamma\text{-CD})_6$, is composed of six ɤ-CD tori. A large spherical pore of 1.7 nm in diameter exists at the center of each $(\gamma\text{-CD})_6$ unit, and these units are connected to form the porous framework. The crystal structure of the CD-MOF was body-centered cubic packing of the $(\gamma\text{-CD})_6$ units. Michida et al. [8] investigated the crystallization of CD-MOF with inclusion of ferulic acid and the adsorption behaviors of ferulic acid on CD-MOF. CD-MOF is environmentally benign as it can be produced from starch and identified as most promising material to capture CO_2 [9,10]. In this study, CD-MOF with high BET specific surface area near 1000 m^2g^{-1} was synthesized by vapor diffusion of methanol into a KOH solution of ɤ-CD. Adsorption and desorption properties of CO_2 on CD-MOF were investigated by thermogravimetric analysis.

2. Experimental

2.1. Preparation of CD-MOF

Potassium hydroxide, methanol and dichloromethane were purchased from Wako Chemicals and ɤ-CD was purchased from Tokyo Chemical Industry. First, ɤ-CD (163mg, 0.126 mmol) and KOH (56.11mg, 1 mmol) were dissolved in deionized water (5.0 mL). The solution was then filtered using a syringe filter (pore size, 0.45μm). Filtered clear solution was transferred into a polyvinyl chloride (PVC) tube immersed in a glass jar filled with methanol solution (50 mL). Growth of colourless crystals was then achieved by vapour diffusion of methanol into the solution at room temperature for 14 days in the closed system.

As-synthesized CD-MOF crystals have to be activated by the removal of residual water or starting materials from the pores in the crystals. After the removal of the aqueous solution, the crystals was repeatedly washed by methanol and then dispersed in dichloromethane. The washing process of crystals with dichloromethane was repeated for three times in a period of three days. Crystals were highly vacuumed and dried in an oven for 60°C for 1 day. The yield of CD-MOF was 77.3%.

2.2. Characterization of CD-MOF

The surface morphology of CD-MOF was observed with scanning electron microscope (SEM, Keyence, VE-9800). Powder X-ray diffraction (PXRD) analysis was conducted with an X-ray diffractometer (Rigaku, Cu-Ka radiation) to characterize the crystalline structure of CD-MOF. Brunauer-Emmett-Teller (BET) specific surface area and the mean porous equivalent diameter of guest-free CD-MOF samples were measured with the surface area and porosity analyzer (Tristar II, Shimadzu) with the standard nitrogen adsorption-desorption system at -196°C (77K) after degassed under vacuum at 45°C. Thermogravimetric analysis (TGA) was conducted with thermal analysis device (Hitachi, TG/DTA 7220) to determine the adsorption amount of CO_2 from the change in the weight as a function of time and temperature in pure CO_2 and in mixture of CO_2 with Ar.

3. Results and Discussions

As shown in Fig.1 (a), colourless cubic crystals with a dimension of 3 μm on each side were formed after vapour diffusion of 14 days. PXRD pattern of as-synthesized (Fig.1 (b)) and solvent-free (Fig.1 (c)) CD-MOF were consistent with that of previous findings [6,7], which provides confirmation of CD-MOF crystal structure. In addition, the resultant CD-MOF possess BJH pore volume of 0.463 cm^3/g, a remarkably high BET surface area of 970.3 m^2/g and an average pore size of 1.9 nm, indicating the formation of micropore.

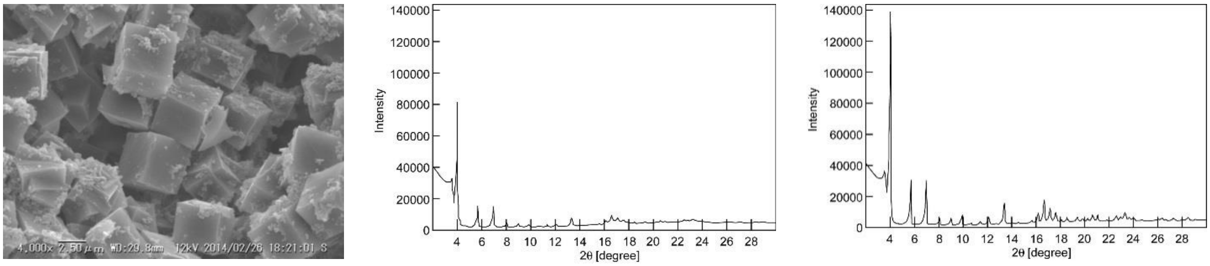

Fig. 1. (a) SEM image of CD-MOF with magnification of 4,000; (b) Powder X-ray diffraction patterns for as-synthesized CD-MOF and (c) evacuated CD-MOF

In order to validate CO_2 adsorption on CD-MOF, yellow crystalline samples prepared by introducing a methyl red indicator were exposed to a CO_2-rich atmosphere; both dry gas from CO_2 cylinder and humid CO_2 gas evolved from sublimation of dry ice. A colour change from yellow to orange/red for pH responsive CD-MOF was observed regardless of the CO_2 source, indicating the properties of CD-MOF have changed from basic state to acidic state after the exposure of CO_2. Fig. 2 shows the estimated reaction scheme between CO_2 and ɤ -CD in CD-MOF crystal. Prior to the exposure of CO_2, a basic environment was formed by free hydroxide ion existed in CD-MOF. When CO_2 was introduced into CD-MOF crystal, hydroxyl groups located on ɤ-CD torus reacts to CO_2 forming carbonic acid, which caused the proton liberation. As a result, acid environment was formed in CD-MOF and colour of pH responsive CD-MOF changed red due to deprotonation of methyl red. Reversibility of CO_2 adsorption behavior on CD-MOF was also tested to ensure it is applicable for carbon fixation, effective CO_2 desorption for the transportation to the storage site and cycle operation through adsorption and desorption process. The colour of CD-MOF was reverted back to yellow in ambient air condition, indicating that the transient carbonic acid had converted back to OH group and CO_2 was released.

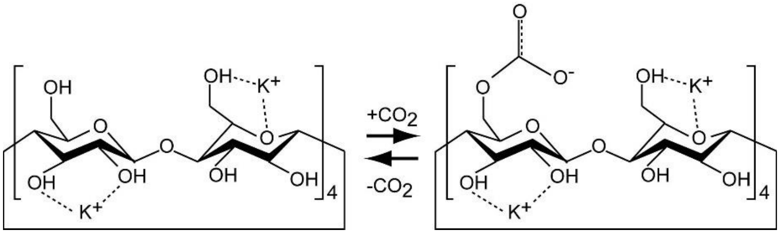

Fig. 2. Chemical reaction between CO_2 and ɤ-CD in CD-MOF

Quantitative analysis for measurement of CO_2 uptake was carried out by TGA by using pure CO_2. The adsorption amount of CO_2 on the complete evacuated CD-MOF sample reached 24 mg-CO_2/g-CD-MOF. Meanwhile the adsorption amount was drastically decreased when using the incomplete evacuated CD-MOF sample, having the BET specific surface area of less than 400 $m^2 \cdot g^{-1}$. The recyclability test of CD-MOF was carried out by switching the adsorption step (CO_2 flow at 30°C) to the desorption step (Ar flow at 60°C) in the multiple CO_2 adsorption-desorption process. As shown in Fig.3, the adsorption amount of CO_2 was slightly decreased with the number of cycle operations through adsorption-desorption process. The reduction of CO_2 adsorption capacity might be caused by the remaining of CO_2 in the CD-MOF after desorption due to the low desorption rate.

By using a binary gas mixture of 25 vol% CO_2 and 75 vol% Ar at 30°C, the adsorption amount of CO_2 was also determined from the measurement of TGA. The value of the adsorption amount (24 mg-CO_2/g-CD-MOF) was almost coincident with that in pure CO_2. This saturated adsorption amount means that the number of the adsorbed CO_2 molecule per a ɤ-CD molecule forming CD-MOF crystal is 0.7. CD-MOF has a large free space to adsorb CO_2 under the condition of a high pressure CO_2 adsorption.

Effect of the system temperature on the adsorption amount on CD-MOF was investigated at 30-60°C. The activation energy required for CO_2 adsorption on CD-MOF was -58.22 $kJ \cdot mol^{-1}$ which was close to the enthalpy of reaction for the bicarbonate formation (-66.4 $kJ \cdot mol^{-1}$ at 25°C) according to Wu et al. [10]. Therefore, it was further proven that the main adsorption mechanism is the chemisorption of CO_2 by interacting with the most reactive primary hydroxyl groups located on each individual ɤ-CD torus, hence forming carbonic acid.

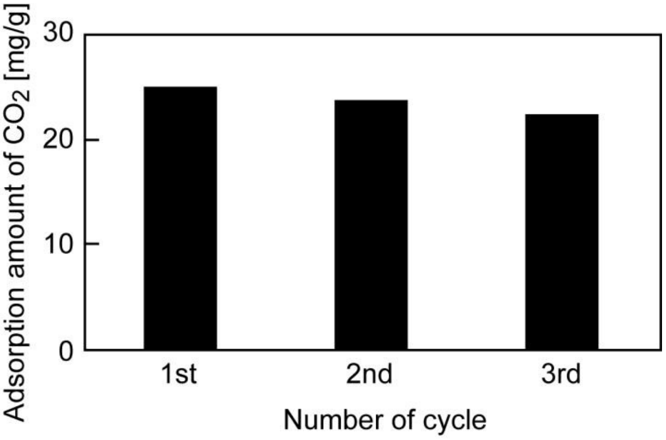

Fig. 3. Adsorption amount of CO_2 on CD-MOF against the number of cycle operations through adsorption-desorption process

4. Conclusion

The CO_2 adsorption behavior on CD-MOF was evaluated both qualitatively and quantitatively. The results confirmed the chemical sorption of CO_2, indicating the formation of reversible carbonic acid by the interaction of hydroxyl groups on the ɤ-CD torus in CD-MOF with CO_2. The adsorption amount of CO_2 in pure CO_2 gas or 25vol% CO_2 in Ar gas was 24 mg-CO_2/g-CD-MOF at 30°C. CD-MOF was found to be promising material for CO_2 capture and separation. Future work is required to understand the high pressure CO_2 adsorption and to separate CO_2 form the mixture of CO_2/N_2 or CO_2/CH_4.

Acknowledgements

The authors gratefully acknowledge Sojo University, Japan and Universiti Teknologi Petronas, Malaysia for the financial support for the collaborative research program.

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