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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.

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Keywords: CD-MOF; CO_2 adsorption; cyclodextrin

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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, $(ɤ\text{-CD})_6$, is composed of six ɤ-CD tori. A large spherical pore of 1.7 nm in diameter exists at the center of each $(ɤ\text{-CD})_6$ 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 $(ɤ\text{-CD})_6$ 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