Catalysis Today 185 (2012) 35–40

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

# $CO_2$ adsorption and catalytic application of Co-MOF-74 synthesized by microwave heating

Hye-Young Cho[a], Da-Ae Yang[a], Jun Kim[a], Soon-Yong Jeong[b], Wha-Seung Ahn[a,*]

[a] *Department of Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea*
[b] *Applied Chemistry and Engineering Division, KRICT, Yuseong 305-600, Republic of Korea*

## ARTICLE INFO

*Article history:*
Received 31 May 2011
Received in revised form 1 August 2011
Accepted 9 August 2011
Available online 30 August 2011

*Keywords:*
Co-MOF-74
Microwave heating
$CO_2$ adsorption
$CO_2$ cycloaddition
Styrene oxide

## ABSTRACT

High-quality Co-MOF-74 crystals were successfully synthesized in 1 h by microwave heating (Co-MOF-74(M)). The XRD pattern and textural properties of Co-MOF-74(M) including the BET surface area (1314 $m^2 g^{-1}$) were virtually identical to those of a sample synthesized in 24 h by the solvothermal method (Co-MOF-74(S), 1327 $m^2 g^{-1}$). Average particle size of the former (*ca.* 50 μm long and 8 μm wide) was, however, significantly smaller than that of the latter (*ca.* 300 μm long and 70 μm wide). The $H_2O$ adsorption capacities of the crystals at 25 °C were 466 and 605 mg $g^{-1}$ for Co-MOF-74(M) and Co-MOF-74(S), respectively. The adsorption isotherms of Co-MOF-74(M) for $CO_2$ and $N_2$ showed a high $CO_2$ adsorption capacity (288 mg $g^{-1}$) and excellent selectivity over $N_2$ (>25:1) at 25 °C. Eight consecutive adsorption–desorption cycles established that there was no deterioration in the adsorption capacity, which showed reversible adsorbent regeneration at 100 °C under He flow for a total duration of 1100 min. Co-MOF-74(M) also demonstrated excellent catalytic performance in cycloaddition of $CO_2$ to styrene oxide under relatively mild reaction conditions (2.0 MPa, 100 °C) with close to 100% selectivity to carbonate confirmed by GC–MS, $^1$H NMR, and FT-IR. Styrene oxide conversion increased with $CO_2$ pressure and reaction temperature. No appreciable effect of catalyst particle size was detected, and Co-MOF-74(M) could be reused 3 times without loss of catalytic activity and with no structural deterioration.

## 1. Introduction

There has been a rapid growth in research activities worldwide for $CO_2$ capture, storage, and utilization (CSU), spurred by increasing awareness of the link between $CO_2$ accumulation in the atmosphere and global warming [1]. The most common method for $CO_2$ capture is gas absorption, monoethanol amine (MEA) being the most widely used solvent. However, the amine based systems for $CO_2$ removal suffer from a high energy requirement for regeneration as well as corrosion problems [2]. Thus, alternative $CO_2$ processes for $CO_2$ capture via adsorption on solid media need consideration. For this purpose, zeolites [3], activated carbons [4], hydrotalcite-like compounds [5], and metal oxides [6] have been investigated, and metal organic frameworks (MOFs) are currently receiving wide attention as an adsorbent material for future application [7].

$CO_2$ is an attractive $C_1$ building block in organic synthesis [8]. However, due to the inert nature of $CO_2$, efficient catalytic chemical fixation remains a significant synthetic challenge [9]. One of the most promising methodologies in this area is the synthesis of cyclic carbonates via the metal-catalyzed coupling of $CO_2$ and epoxides [10,11], which are valuable as monomers, aprotic polar solvents, pharmaceutical/fine chemical intermediates, and for many biomedical applications [12,13]. Various catalysts have been developed for the cycloaddition of $CO_2$, but the effective catalysts are generally homogeneous and require a co-catalyst. To overcome the separation problem, several heterogeneous catalysts have also been suggested [14–19], but most of them suffer the inherent problem of lower activity [19]. It remains to be seen if a heterogeneous catalyst that is efficient under mild reaction conditions can be proposed.

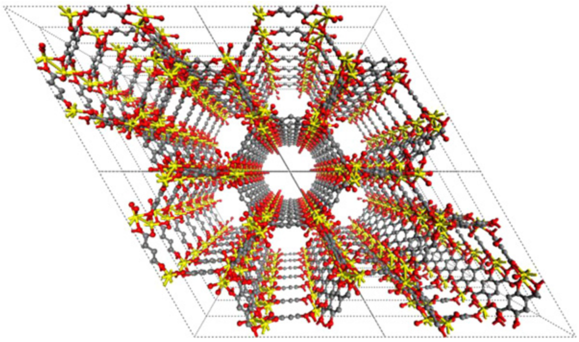
Metal-organic frameworks (MOFs) are made of metal ions or clusters interconnected by organic ligands [20]. They have great potential as adsorbents/catalysts due to their extremely large surface area, well-ordered porous structures, and diverse means available for functionalization. Various applications, including gas storage, separation, magnetism, and catalysis have been developed, including $CO_2$ adsorption and heterogeneous catalysts for fine chemicals [21–23].

The crystal structure of the MOF-74 in Scheme 1 is built around a 1-D honeycomb motif with pores of 1.1–1.2 nm diameter and helical chains of edge-condensed metal–oxygen coordination octahedrals located at the intersections of the honeycomb, in which the metal is square–pyramidally coordinated [24]. One of the six

---

* Corresponding author. Tel.: +82 32 860 7466; fax: +82 32 872 0959.
*E-mail address:* whasahn@inha.ac.kr (W.-S. Ahn).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.08.019



**Scheme 1.** The structure of Co-MOF-74 used in this work (carbon atoms, gray; oxygen atoms, red; cobalt atoms, yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

oxygen atoms coordinated to the metal comes from a solvent water molecule, and the MOF-74 structure develops coordinatively unsaturated (open) metal sites in Lewis acidity upon removal of the solvent molecules attached to the metal sites by heating in vacuum. Co-MOF-74 is one of the MOF-74 series, which can be prepared by replacing the typical zinc atoms with cobalt in the MOF-74 structure [25,26].

In this work, Co-MOF-74 samples were synthesized by the alternative microwave-eating method, and their physicochemical properties were compared against those of a sample prepared by the conventional solvothermal method. The Co-MOF-74 samples were then examined for their adsorption properties for $CO_2$ and water vapor. Finally, their potential application as a heterogeneous catalyst for high-pressure cycloaddition reaction of $CO_2$ to styrene oxide was investigated for the first time. It will be very meaningful for CSU work if Co-MOF-74 is proven effective both as a carbon dioxide adsorbent and as a catalyst for its chemical fixation.

## 2. Experimental

### 2.1. Microwave synthesis of Co-MOF-74

First, 0.148 mmol of cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma–Aldrich) and 0.044 mmol of 2,5-dihydroxy benzenedicarboxylic acid ($H_4DHBDC$, Sigma–Aldrich) were dissolved in 18 mL of a mixed solvent (DMF:ethanol:water = 1:1:1 (v/v/v)) and put into a 35 mL tube, which was sealed with a rubber septum and placed in a microwave oven (Discover S-class, CEM, Maximum power of 300 W). The resulting mixture was heated to 130 °C, held for 1 h, and then cooled to room temperature. For comparison, Co-MOF-74 was also synthesized by the conventional solvothermal method following a procedure reported in the literature [26]; synthesis details are described in Supporting information (SI). The red-orange crystals were separated by centrifugation. After washing three times with *N*,*N*′-dimethylformamide (DMF, Sigma–Aldrich), they were placed in methanol, which was decanted and replenished four times for two days. The solvent was removed under vacuum at 250 °C for 5 h, yielding a dark-purple porous material. The activated materials were stored in a desiccator under vacuum.

### 2.2. Characterization

XRD patterns of the Co-MOF-74 samples were obtained on a Rigaku diffractometer using CuK$\alpha$ ($\lambda = 1.54$ Å) radiation. $N_2$ adsorption/desorption isotherms were obtained on an ASAP-2020 (Micromeretics, USA) sorptometer at liquid nitrogen temperature. The samples were degassed at 250 °C for 5 h ($3 \times 10^{-3}$ torr) prior to adsorption. The specific surface areas of the samples were calculated by the BET method. Morphological features were examined by SEM (Hitachi S-4200). The thermal stability of the samples was evaluated using a thermogravimetric analyzer (TGA, SCINCO thermal gravimeter S-1000); 10 mg of each sample was heated at 10 °C $min^{-1}$ to 600 °C under air flow (30 mL $min^{-1}$).

### 2.3. Water vapor adsorption measurement

Water vapor adsorption measurement was conducted using a BELSORP-Max (BEL, JAPAN) at 25 °C ($P_0 = 3.169$ kPa). Water vapor was developed by vaporizing water under ultra-high vacuum at 40 °C, which was purified through soaking procedures by repeatedly freezing the water using liquid nitrogen and consequently melting the water and evacuating bubbles of other dissolved matters. Prior to the water vapor adsorption test, samples were evacuated through the same pretreatment procedure as for the $N_2$ adsorption.

### 2.4. $CO_2$ and $N_2$ adsorption measurement

$CO_2$ and $N_2$ sorption isotherms under static conditions were obtained by means of a BELsorp(II)-mini (BEL, Japan) at 0 °C and 25 °C using activated solid samples. The experimental adsorption data were fitted to the Langmuir–Freundlich equation, and the heat of adsorption was then calculated by applying the Clausius–Clapeyron equation. $CO_2$ desorption and adsorption/desorption cyclic experiments were conducted using a TGA unit connected to a gas flow panel. Ultra-high purity He was used as a purge gas in the initial activation and desorption experiments, and adsorption was carried out using ultra-high purity $CO_2$ (99.999%). A feed flow rate of 30 mL $min^{-1}$ to the sample chamber was controlled using an MFC.

### 2.5. Cycloaddition of $CO_2$ to styrene oxide

Styrene oxide (5 mmol) and Co-MOF-74 (20 mg) were mixed in chlorobenzene (30 mL) and put into a 100 mL stainless steel high-pressure reactor. Prior to reaction, the catalyst Co-MOF-74 was dried at 100 °C for 1 h under vacuum and then immediately transferred to the reactor. The temperature of the reactor was increased and maintained at 100 °C, and the reactor was pressurized with $CO_2$ (99.999%) up to 2.0 MPa. The reaction vessel was kept connected to a $CO_2$ source throughout the reaction via a one-way check valve to maintain the pressure at the desired level. The reaction mixture was stirred (200 rpm) under the pressurized conditions for a period of 0.5–4 h. When the reaction was completed, the reactor was quickly cooled down in cold water, and then pressure was released slowly. After catalyst separation by centrifugation, conversion, selectivity, and product yield were determined by GC (Agilent 7890, HP-5 column; 30 m, 0.320 mm, 0.25 $\mu$m). The cyclic carbonate was isolated by removing chlorobenzene solvent at 80 °C under vacuum, and the products were washed with dichloromethane 3 times in an $N_2$ environment. The structure of the product was determined by GC–MS (Varian 1200L with 3800GC), $^1H$ NMR (Varian Inova 400, 400 MHz using $CDCl_3$ as solvent), and FT-IR (Nicolet iS10 FT-IR spectrometer). The separated catalyst was washed with acetone 3 times and dried at 100 °C for 2 h under vacuum for reuse.

## 3. Results and discussion

### 3.1. Microwave synthesis of Co-MOF-74

Fig. 1 compares the XRD pattern (a), $N_2$ adsorption-desorption isotherm (b), and thermal stability (c) of the Co-MOF-74 sample synthesized by microwave heating at optimum condition (hereafter, Co-MOF-74(M)) with those prepared by solvothermal