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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 CO₂ adsorption CO₂ 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 m² g⁻¹) were virtually identical to those of a sample synthesized in 24 h by the solvothermal method (Co-MOF-74(S), 1327 m² g⁻¹). Average particle size of the former (*ca.* 50 μ m long and 8 μ m wide) was, however, significantly smaller than that of the latter (*ca.* 300 μ m long and 70 μ m wide). The H₂O 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 CO₂ and N₂ showed a high CO₂ adsorption capacity (288 mg g⁻¹) and excellent selectivity over N₂ (>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 CO₂ to styrene oxide under relatively mild reaction conditions (2.0 MPa, 100 °C) with close to 100% selectivity to carbonate confirmed by GC–MS, ¹H NMR, and FT-IR. Styrene oxide conversion increased with CO₂ 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.

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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 CO₂ 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 CO₂ and water vapor. Finally, their potential application as a heterogeneous catalyst for high-pressure cycloaddition reaction of CO₂ to styrene oxide was investigated for the first time. It will be very meaning-ful 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(NO₃)₂·6H₂O, Sigma-Aldrich) and 0.044 mmol of 2,5-dihydroxy benzenedicarboxylic acid (H₄DHBDC, 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 300W). 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 α (λ = 1.54 Å) radiation. N₂ 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 × 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 $10 \,^{\circ}$ C min⁻¹ to 600 $^{\circ}$ 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 N₂ 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 CO₂ 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 highpressure 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 CO₂ (99.999%) up to 2.0 MPa. The reaction vessel was kept connected to a CO₂ 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 µm). 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 N2 environment. The structure of the product was determined by GC-MS (Varian 1200L with 3800GC), ¹H NMR (Varian Inova 400, 400 MHz using CDCl₃ 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

Table 1

Textural properties of Co-MOF-74(S) and Co-MOF-74 (M).

Samples	$S_{\text{BET}} (m^2 g^{-1})$	$V_{\rm Pore}~({\rm cm}^3{\rm g}^{-1})$	$S_{\rm Ext} ({\rm m}^2{\rm g}^{-1})$	S_{Micro} (m ² g ⁻¹)	Product yield (%)
Co-MOF-74(S)	1327	0.52	9	1318	68
Co-MOF-74(M)	1314	0.51	20	1294	76

Table 2

Textural properties of Co-MOF-74(M) synthesized at different conditions.

Conditions			S_{BET} (m ² g ⁻¹)	$V_{\rm Pore} ({\rm cm}^3 {\rm g}^{-1})$	Product yield (%)	
Temperature (°C)	Power (W)	Time (min)				
100	180	60	1318	0.49	7	
120	180	60	1319	0.51	45	
	120	60	1402	0.71	58	
	150	60	1411	0.69	63	
130	180	30	1193	0.49	69	
	180	40	1155	0.47	75	
	180	60	1314	0.51	76	
	180	70	1273	0.51	74	
	210	30	123	0.01	84	
	210	40	1270	0.65	72	
	210	60	1321	0.50	74	



Fig. 1. (A) Powder XRD, (B) N₂ sorption isotherms at -196 °C, and (C) TGA profiles of Co-MOF-74(S) and Co-MOF-74(M) samples.



Fig. 2. SEM images of (A) Co-MOF-74(S) and (B) Co-MOF-74 (M).

method (hereafter, Co-MOF-74(S)). The XRD patterns of Co-MOF-74(M) and Co-MOF-74(S) (Fig. 1a) were very close to each other and were in good agreement with the pattern reported by Dietzel et al. [25]. Both samples exhibited type I isotherms in N₂ adsorption isotherms at -196°C with no hysteresis, and the BET surface area of Co-MOF-74(M) was $1314 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of 0.51 cm³ g⁻¹, whereas the corresponding values for Co-MOF-74(S) were $1327 \text{ m}^2 \text{ g}^{-1}$ and $0.52 \text{ cm}^3 \text{ g}^{-1}$, respectively (Table 1). The XRD patterns of Co-MOF-74(M) samples prepared under various microwave synthesis conditions (synthesis temperature, microwave irradiation power level, and synthesis time) are shown in Fig. S1, and the corresponding textural properties of Co-MOF-74(M) under various synthesis conditions are summarized in Table 2. According to the results, the optimized Co-MOF-74(M) was synthesized at 130 °C with 180W microwave power level for 1 h, which resulted in the highest surface area with a reasonably high product yield (ca. 76% based on ligand). Co-MOF-74(S), on the other hand, resulted in a somewhat lower crystal yield (68%). Fig. 1c shows TGA profiles of Co-MOF-74(S) and Co-MOF-74(M). The first weight loss up to 150 °C can be attributed to the solvent used for synthesis (H₂O and ethanol) and washing (methanol) removal from the cavities, whereas the second weight loss around 200 °C is due to the removal of guest molecules from open metal sites on Co-MOF-74. The TGA pattern comprising two-step weight reduction is a unique feature of porous MOF materials having open metal sites [25]. Co-MOF-74(S) showed the final weight loss in a temperature range from 280 °C to 300 °C due to structural collapse, and the final collapse for Co-MOF-74(M) occurred at a slightly higher temperature

Fig. 2 shows SEM images of Co-MOF-74(S) and Co-MOF-74(M). Both samples were made of single-phase hexagonal columnstructured particles with long aspect ratios but Co-MOF-74(S) (ca. $300 \,\mu\text{m}$ long and $70 \,\mu\text{m}$ wide) was significantly larger than Co-MOF-74(M) (ca. 50 µm long and 8 µm wide). This difference in particle size also resulted in a larger external surface area for Co-MOF-74(M) (Table 1). Microwave synthesis has been widely applied in inorganic materials synthesis due to the benefits of rapid synthesis kinetics, uniform particle morphology, and phase purity [27]. An applied oscillating electric field in the microwave approach is coupled with the permanent dipole moment of the molecules in the synthesis medium, inducing molecular rotations - resulting in rapid heating of the liquid phase [28]. In microwave synthesis, the average particle size of the product is typically smaller than that of solvothermal synthesis because the short reaction time limits particle growth, while nucleation is not hindered.

3.2. Water vapor adsorption measurement

Water adsorption isotherms of Co-MOF-74(S) and Co-MOF-74(M) are shown in Fig. 3. Both of them adsorbed water vapor



Fig. 3. Water vapor adsorption-desorption isotherms at 25 °C.

reversibly through a single step. This presumably reflects the fact that Co-MOF-74 is composed of only one type of pore in uniform 1-D hexagonal channels, and the pores did not cause hysteresis toward water vapor. The isotherms quickly rising at the low pressure region ($P/P_0 < 0.1$) indicate the hydrophilic character of open metal sites (Lewis acidic sites) in Co-MOF-74, and well lined-up oxygen sites between organic ligands and metal complex enhance binding water molecules via hydrogen bonding. Water adsorption subsequently becomes saturated as the P/P_0 increases, which reflects the hydrophobic charater of Co-MOF-74 due to benzene rings that comprise the micropores [29]. Zeolite 13X and activated carbons are well known for their water vapor adsorption properties [30,31], and the water adsorption properties of commercial zeolite 13X (Sigma-Aldrich) and activated carbon (G-80, Darco) were also plotted for comparison. Co-MOF-74 clearly demonstrated a higher affinity toward water vapor than zeolite 13X and activated carbon, largely due to the regularly arranged oxygens connected to benzene rings and the open metal sites showing strong Lewis acidity. Interestingly, the water adsorption capacity of Co-MOF-74(S), 605 mg g^{-1} , was significantly higher than that of Co-MOF-74(M), 466 mg g⁻¹. While it was reported previously that even same materials could possess different surface characteristics if they are prepared via different routes [32,33], it is also plausible that the particle size differences of the two samples had also an influence over the water sorption behaviour; longer 1-D channels in Co-MOF-74(S) could accommodate extra water molecules via intermolecular attraction. Stability of MOF-74 in steam was reported to be superior to those of other metal organic framework (MOF) structures [34].



Fig. 4. (A) CO₂ and N₂ sorption isotherms of Co-MOF-74(M) at 0 °C and 25 °C and (B) the corresponding heat of adsorption.

Table 3

Effect of reaction conditions in catalytic CO₂ coupling reaction of styrene oxide.

Catalyst	Pressure (MPa)	Temperature (°C)	Time (h)	Conversion (%)
Co-MOF-74(M)	2.0	60	4	38
Co-MOF-74(M)	2.0	80	4	78
Co-MOF-74(M)	2.0	100	4	96
Co-MOF-74(M) 1st recycle	2.0	100	4	95
Co-MOF-74(M) 2nd recycle	2.0	100	4	95
Co-MOF-74(M)	1.0	100	4	49
Without catalyst	2.0	100	4	0

Reaction conditions: chlorobenzene 30 mL, styrene oxide 5 mmol, and catalyst 20 mg.

Table 4

Comparison with other catalytic systems on cycloaddition reaction of CO₂ to styrene oxide.

Catalyst	co-Catalyst	Ratio ^a	Pressure (MPa)	Temperature (°C)	Time (h)	Yield (%)	Ref.
Co-complex ^b	DMAP ^c	1:1(:2)	2.0	120	3	85.8	[15]
MOF-5	n-Bu ₄ NBr ^d	24:1(:3)	0.1	50	15	92.0	[19]
$Zn_3[Co(CN)_6]_2$	n-Bu ₄ NCl ^e	60:1(:2)	0.4	140	6	97.0	[14]
Ion-exchanged resin	-	12:1	8.0	100	12	95.2	[16]
n-Bu ₄ NBr supported SiO ₂	-	60:1	8.0	150	8	97.0	[17]
Mg–Al oxide ^f	-	1:1	0.5	120	15	90.0	[18]
Co-MOF-74	-	30:1	2.0	100	4	96.0	Present work

^a Ratio = substrate:catalyst (:co-Catalyst).

^b Co-complex, cobalt-tetraamidomacrocyclic complex.

^c DMAP, 4-dimethylamonopyridine.

^d *n*-Bu₄NBr, tetrabutylammonium bromide.

^e n-Bu₄NCl, tetrabutylammonium chloride.

^f DMF was used as solvent.

Divit was used as solvent.



Fig. 5. CO₂ adsorption–desorption recycling test of Co-MOF-74(M) using highpurity CO₂.

3.3. CO_2 and N_2 adsorption measurement

Adsorption and desorption equilibrium isotherms of CO₂ and N₂ on Co-MOF-74(M) at 0 °C and 25 °C are plotted in Fig. 4a. Virtually identical isotherms obtained for Co-MOF-74(S) are not shown. The steepness of the slope in the low-pressure region of the CO₂ adsorption isotherm indicates strong adsorption of CO₂ onto Co-MOF-74(M), while that of the N₂ isotherms is quite linear and exhibits low uptake, signaling a weak interaction between N₂ and the adsorbent. Up to 288 mg g^{-1} of CO₂ uptake was obtained at 25 °C and 1 bar, which is significantly higher than the adsorption capacities of other inorganic adsorbents including the amine-functionalized ones [35]. The N₂ uptake at 25 °C, on the other hand, was only 1.7 mg g⁻¹ at 1 bar. As a result, the selectivity of CO₂ over N₂ in Co-MOF-74(M) was very high (CO₂:N₂ = 25:1); CO₂ was more strongly adsorbed than N₂ because of the significantly stronger quadruple moment of CO₂ in comparison to N₂.

Fig. 4b shows the corresponding heats of CO_2 adsorption over coverage, which decreases sharply with the loading amount (from *ca*. 51 to 29.5 kJ mol⁻¹); at the low surface coverage, CO_2 molecules are preferably adsorbed onto the most energetic adsorption sites of open metal Lewis acid character. As loading increases, these



Fig. 6. Effect of reaction time on the catalytic activity of Co-MOF-74(S) and Co-MOF-74(M) in cycloaddition of CO_2 to styrene oxide at 100 °C and 2.0 MPa.

sites become saturated, and the adsorbate-adsorbent interaction becomes governed mainly by dispersion [36,37].

Stability of the adsorbent is another important parameter to be considered. Fig. 5 shows the CO₂ adsorption–desorption recycling performance of Co-MOF-74(M) in eight consecutive adsorption–desorption runs; close CO₂ adsorption capacity (210 mg g⁻¹) to the value measured by the static equilibrium adsorption isotherm was measured. The adsorbed CO₂ at 25 °C could be completely desorbed at 100 °C; 92%, 95%, and 97% of CO₂ was found to be desorbed at 25 °C, 50 °C, and 75 °C, respectively. No deterioration in adsorption capacity was detected, and excellent regeneration and adsorption–desorption stability were observed for a total duration of 1100 min.

3.4. Cycloaddition of CO₂ to styrene oxide

The catalytic property of Co-MOF-74 was tested for the cycloaddition reaction of CO_2 to styrene oxide. As shown in Fig. 6, styrene oxide conversion steadily increased from 41% to 96% as the reaction time elapsed from 0.5 to 4 h at 100 °C and 2.0 MPa CO_2 pressure condition over Co-MOF-74 in chlorobenzene. A single product of 4-phenyl-1,3-dioxolan-2-one was obtained, as confirmed by FT-IR and ¹H NMR in Figs. S2 and S3, respectively [14]. It was also established that both Co-MOF-74(M) and Co-MOF-74(S), despite significantly different particle sizes, produced very similar conversion profiles, implying that negligible pore diffusion affects the reaction rates under the given set of reaction conditions.

As shown in Table 3, styrene oxide conversion increased from 38% to 96% as the temperature increased from 60 °C to 100 °C, and the conversion decreased from 96% to 49% as the CO₂ pressure was reduced from 2.0 MPa to 1.0 MPa. Apparently, the concentration of CO₂ dissolved in chlorobenzene increased at higher pressure, which in turn increased the reaction rates in the liquid phase. To assess the stability of Co-MOF-74(M) during the liquid phase reaction, a catalyst recycling test was conducted at 100 °C. At the end of reaction, the catalyst was recovered by filtration, washed with acetone, activated at 100 °C under vacuum for 2 h to remove the adsorbed species, and then reused. As shown in Table 3, styrene oxide conversions for 3 repeated runs produced virtually constant values. Powder XRD patterns of the fresh catalyst and those after the second and third runs were also measured (Fig. S4). These showed almost identical diffraction patterns with the same intensity and indicated that the structural integrity of Co-MOF-74 was maintained during the reaction. The reaction did not occur without a catalyst.

Previous reports on the synthesis of cyclic carbonate from CO_2 and epoxide suggested that concurrent presence of both Lewis base sites and Lewis acid sites are desirable for the reaction [10]; the former activate CO_2 , which then attacks styrene oxide adsorbed on the latter. We believe that the six oxygen atoms (five oxygen atoms from the ligand and one from H_2O used as solvent) located around cobalt atoms function as a base, whereas open metal cobalt is well known to function as a Lewis acid. We compared our results with the activity of several other catalyst systems reported in the literature for the same reaction in Table 4. We found that Co-MOF-74 is indeed very promising as a catalyst for cycloaddition reaction in two respects; a co-catalyst, such as quaternary ammonium salt is not needed, and the reaction proceeds under relatively mild reaction conditions of lower pressure and temperature than others.

4. Conclusions

High-quality Co-MOF-74 crystals were obtained by a microwave-heating method in 1 h accompanied by a substantial reduction in crystal size. The synthesized Co-MOF-74 showed both high CO₂ and water vapor sorption capacities (288 and 466 mg g⁻¹, respectively) and high selectivity against N₂ (>25) at 25 °C. Co-MOF-74 having Lewis acid sites also exhibited excellent catalytic performance in cycloaddition of CO₂ to styrene oxide without any co-catalyst under relatively mild conditions: 96% yield in carbonate at 2.0 MPa of CO₂ and 100 °C. Co-MOF-74 catalysts were reusable several times with retention of high catalytic activity.

Acknowledgements

This work was supported by the Carbon Dioxide Reduction & Sequestration R&D Center (CDRS) in Korea and by the KRICT OASIS Project from Korea Research Institute of Chemical Technology.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.08.019.

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