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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A Novel Metalloporphyrin-based Conjugated Microporous Polymer for Capture and Conversion of CO₂

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A novel conjugated microporous polymer was solvothermally synthesized using an aluminum porphyrin as a main building block, which had a high Brunauer-Emmett-Teller specific surface area up to 839 m² g⁻¹ and a pore volume of 2.14 cm³ g⁻¹. The polymer displayed excellent capacity to capture carbon dioxide (4.3 wt%) at 273 K and 1 bar, and good catalytic activity for cyclic carbonate synthesis with TOF up to 364 h⁻¹.

Induction

There is much environmental concern about the increasing levels of atmospheric carbon dioxide (CO₂) which is suspected to be a primary factor in global climate change.¹ Thus, CO₂ capture and sequestration (CCS) technologies have been developed to effectively reduce its accumulation in the atmosphere during the past decade.² Due to the drawbacks of high energy demands for chemical sorption method of CO₂ in industry, researchers pay much attention to develop alternative approaches for CCS. Numerous porous materials, such as zeolites,³ activated carbons⁴ and metal-organic frameworks (MOFs),⁵ have been found to effectively capture CO₂, which exhibit great potential in industrial applications.

On the other hand, chemical conversion of captured CO₂ to large scale chemicals is attractive since it is an abundant, inexpensive and nontoxic C1 resource. One of the chemicals is cyclic carbonate formed from cycloaddition of CO₂ and epoxide,⁶ which are widely used as polar aprotic solvent, electrolyte in lithium-ion battery, fuel additive and intermediate for polycarbonate.⁷ Because of high thermodynamic stability of CO₂,⁸ numerous catalyst systems for cyclic carbonate synthesis have been reported,⁹ especially some homogeneous catalyst systems, such as salen metal complexes¹⁰ and metalloporphyrins,¹¹ which show higher catalytic activities under mild conditions compared with heterogeneous catalysts. Recently, Ema's group¹² developed bifunctional porphyrin catalysts, which showed high turnover number numbers (TON = 103,000) for the synthesis of cyclic carbonates. Furthermore, metalloporphyrins are considered to be promising catalysts because the porphyrin framework can be carefully designed, which may provide an opportunity to further enhance catalytic activity. However, these homogeneous catalysts still have difficulty in industrial applications because they are expensive and difficult to be recovered or reused. Thus, it is necessary to develop highly efficient heterogeneous catalysts for synthesizing cyclic carbonates.

Currently, conjugated microporous polymers (CMPs) are of

great interest because of their extraordinarily high surface area, well-defined pore structure and extended π -conjugation effect.¹³ A series of CMPs have been developed for applications in areas such as gas sorption,¹⁴ conducting material,¹⁵ molecular separation¹⁶ and catalysis.¹⁷ For example, metallosalen-based CMPs have been reported, which had high surface area and ability to catalyze the coupling of CO₂ and epoxides in mild reaction conditions.¹⁸ Chen's group prepared a metalloporphyrin-based CMP with high catalytic activity for the oxidation of thiols.¹⁹ Furthermore, Liu *et al.* reported metalloporphyrin based CMPs which displayed excellent CO₂ uptake capacity (up to 13.9 wt%) at 273 K and 1 bar.²⁰ Subsequently, Echegoyen and coworkers developed a new metalloporphyrin based CMP which exhibited very good selectivity for CO₂/CH₄ adsorption.²¹ CMP has the physical backbone and structure of the conjugated framework in addition to the chemical properties of the incorporated metal-organic moieties, which may have capability of not only CO₂ capture but also its simultaneous conversion. CMPs based on metalloporphyrin units have shown good potential for CO₂ capture,²² however, to the best of our knowledge, the catalytic performance of metalloporphyrin-based CMPs for the coupling of CO₂ and epoxides have rarely been explored. It is interesting to develop metalloporphyrin-based CMP for both CO₂ capture and its simultaneous conversion, which also could be recovered from the product easily.

In this study, aluminum porphyrin-based conjugated microporous polymer (Al-CMP) has been solvothermally synthesized. As expected, it is insoluble in common organic solvents and water, and can be recovered from the reaction system easily. The Al-CMP exhibits high surface area, and is capable of capturing and transforming CO₂ to cyclic carbonates in mild reaction conditions.

Experimental

General procedures and methods

All reactions of air- and/or moisture-sensitive complexes and

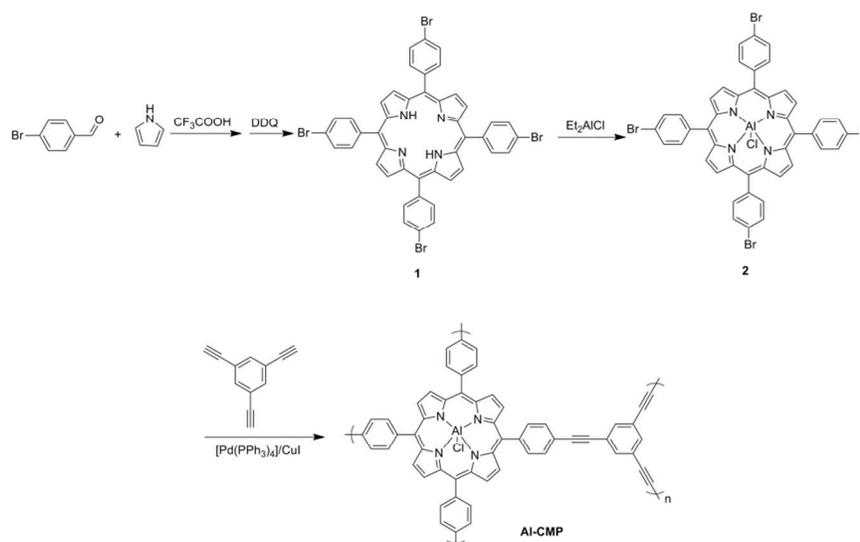
product manipulations were performed under inert atmosphere using standard Schlenk technique or in a glove box. Dichloromethane (CH₂Cl₂), chloroform (CHCl₃), acetonitrile (CH₃CN), pyrrole, propylene oxide (PO) were distilled over CaH₂ under inert atmosphere. The CO₂ gas (99.999%) was purchased and used without further purification. Other chemicals were obtained from Aldrich or Acros, and used as received without further purification unless otherwise stated.

Solution nuclear magnetic resonance (NMR) spectra were recorded at ambient atmosphere using a Bruker ARX-300 spectrometer at room temperature in deuterated chloroform (CDCl₃) or dimethyl sulfoxide (DMSO-d₆), tetramethylsilane (TMS) was used as internal reference. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) was performed on a Bruker atuoflex III mass spectrometer. Fourier transform infrared (FTIR) spectrum was recorded on Bruker Optics Tensor 27 spectrometer. The spectral resolution is 2 cm⁻¹. UV-Visible spectra for complex **2** was recorded on HITACHI U-4100 spectrophotometer using CHCl₃

as the solvent. UV-Visible diffuse-reflection spectra for **Al-CMP** was recorded on SHIMADZU UV-2550 spectrophotometer. ¹H-¹³C CP/MAS solid-state NMR spectra were obtained by a Bruker AVANCE III 400 WB spectrometer. Scanning electron microscopy (SEM) image was obtained on a XL30 ESEM FEG. High-resolution transmission electron microscope (HR-TEM) image was obtained on a Tecnai G2 F20 S-TWIN. Thermogravimetry analysis (TGA) was performed on a Perkin-Elmer Pyris 1 TGA thermal analyzer under a N₂ atmosphere at a heating rate of 10 °C/min from ambient temperature to 800 °C. Inductively coupled plasma (ICP)-optical emission spectroscopy (OES) was performed using a ThermoScientific iCAP6300 instrument. Nitrogen adsorption isotherms at 77 K were measured in liquid nitrogen bath with an Autosorb-IQ2 instrument (Quantachrome). CO₂ adsorption isotherms were measured by a Micromeritic ASAP 2000 instrument at 273 K and 298 K.

Synthetic procedure for Al-CMP

The synthesis of **Al-CMP** is illustrated in Scheme 1.



Scheme 1 Synthesis of Al-CMP.

The detailed synthesis process is listed in the following.

Compound 1. Compound **1** was obtained as reported.²³ A solution of 4-bromobenzaldehyde (1.9 mmol) and pyrrole (1.9 mmol) in 380 mL dry dichloromethane was degassed with a stream of argon for 10 min. The solution was stirred for 1 h after trifluoroacetic acid (0.37 mL) was added, then 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (0.9 g) was added and the solution was stirred for another 1 h. After filtration, the filtrate was concentrated using a rotary evaporator to produce a residue which was purified by column chromatography (silica, petroleum ether/dichloromethane v/v = 1:1) to obtain a purple solid in 22% yield.

¹H NMR(300 MHz, CDCl₃, δ): 8.84 (s, 8H), 8.05 (d, 8H), 7.88 (d, 8H), -2.86 (s, 2H; NH). ¹³C NMR (75 MHz, CDCl₃, δ): 141.00, 135.98, 131.33, 130.15, 122.81, 119.15.

MS (MALDI-TOF): m/z = 926.9 [M+H]⁺ (calcd. 926.9).

Compound 2. A solution of compound **1** (1.0 mmol) in 20 mL dry dichloromethane was degassed with a stream of argon for 5 min in an ice-bath. After 1.3 mmol Et₂AlCl was added slowly, the

reaction solution was heated to room temperature and stirred for 1 h. The mixture was concentrated using a rotary evaporator to produce a residue which was purified by column chromatography (neutral alumina, dichloromethane/methanol v/v = 10:1) and obtained as a purple solid in 97% yield.

¹H NMR(300 MHz, DMSO-d₆, δ): 9.03 (s, 8H), 8.13 (d, 8H), 8.04 (d, 8H). ¹³C NMR (75 MHz, DMSO-d₆, δ): 146.48, 140.03, 135.85, 132.29, 130.07, 122.25, 119.03.

UV(CHCl₃) λ_{max} 419, 518, 549, 589, 631 nm. Elemental analysis for C₄₄H₂₄AlBr₄ClN₄ (990.74): calcd. C 53.34, H 2.44, Al 2.72, Cl 3.58, N 5.66; found C 53.29, H 2.42, Al 2.75, Cl 3.55, N 5.68.

MS (MALDI-TOF): m/z = 950.8 [M-Cl]⁺ (calcd. 950.8).

Al-CMP. **Al-CMP** was obtained as reported.^{18b} Compound **2** (0.57 mmol), 1,3,5-triethylbenzene (180 mg, 1.2 mmol), CuI (50mg) and tetrakis-(triphenylphosphine) palladium(0) (100 mg) were dissolved in a mixture of toluene (15 mL) and triethylamine (6 mL). The reaction mixture was heated to 40 °C and stirred for 1 h under an argon atmosphere (to exclude oxygen and prevent

any homocoupling of the alkyne monomers). Next, the reaction mixture was heated to 80 °C, stirred for 72 h and then cooled to room temperature. The insoluble precipitated polymer was filtered and washed four times with dichloromethane, methanol, water and acetone to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol and dichloromethane (volume ratio = 1:1) for 48 h. The product was dried in a vacuum for 24 h at 70 °C and isolated as a brown powder.

UV λ_{max} 421, 550, 601, 641 nm. Elemental analysis for **Al-CMP** [(C₆₀H₂₈AlClN₄)_n]: calcd. C 83.09, H 3.25, Al 3.11, Cl 4.09, N 6.46; found C 83.15, H 3.79, Al 2.81, Cl 3.63, N 6.52.

Cycloaddition reaction

Propylene oxide, Al-CMP and cocatalyst were added to a stainless-steel autoclave with a magnetic stirrer in a glove box. CO₂ was pressurized to this mixture and the reaction was operated under determined conditions. After reaction, the autoclave was cooled to room temperature, and the CO₂ pressure was released by opening the outlet valve. Then the crude reaction mixture was obtained to calculate the conversion by ¹H NMR spectroscopy in deuterated chloroform.

Results and discussion

Al-CMP Characterization

Al-CMP was synthesized from the reaction of compound **2** with 1,3,5-triethynylbenzene in the presence of a Pd(0) catalyst in toluene. The resultant brown powdery compound had a low density, and was not soluble in any common organic solvents or water. The polymerization process was monitored via IR spectroscopy. Fig.1 displayed the IR spectra before and after polymerization. The disappearance of the C-Br vibrations ($\nu = 483 \text{ cm}^{-1}$) of the starting material indicated both the complete consumption of monomer (compound **2**) and the success of phenyl-alkynyl coupling.

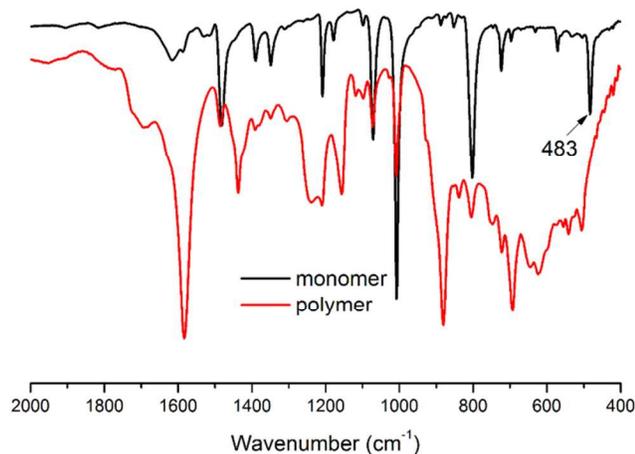


Fig. 1 IR spectra of monomer (compound **2**) and polymer (**Al-CMP**).

The molecular structure of **Al-CMP** was investigated by ¹H-¹³C CP/MAS solid-state nuclear magnetic resonance (NMR). As shown in Fig.2, the peaks at 91.0 and 82.0 ppm were assigned to *sp*-hybridized -C≡C- sites. The peaks at approximately 115.0-150 ppm were ascribed to the carbon atoms of the aromatic rings

in the polymer. Therefore, these results clearly indicated that the cross-coupling of compound **2** and 1,3,5-triethynylbenzene formed a conjugated polymer.

The morphological structure of **Al-CMP** was investigated by SEM and HR-TEM, as shown in Fig.3. The SEM image of **Al-CMP** showed very small granules with an average size of 47 nm. According to the HR-TEM image, nanometer-sized pores were presented in the bulk of the polymer.

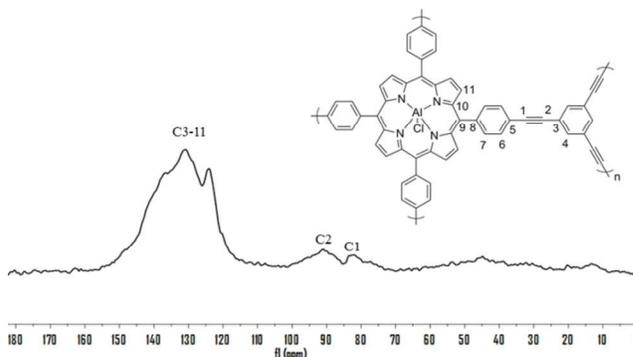


Fig. 2 Solid-state ¹H-¹³C CP/MAS NMR spectra of **Al-CMP** recorded at a spinning speed of 8 kHz.

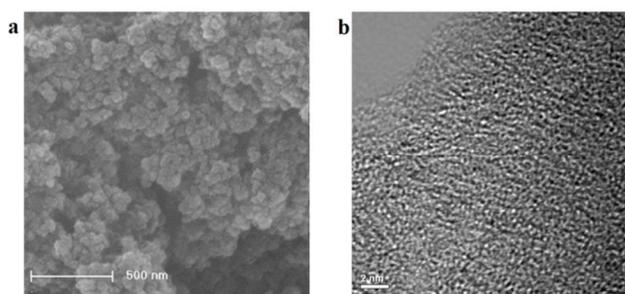


Fig. 3 SEM (a) and HR-TEM (b) of **Al-CMP**.

The porous properties of **Al-CMP** were investigated by nitrogen adsorption analyses at 77 K. According to IUPAC classification, **Al-CMP** showed type I nitrogen adsorption isotherms as shown in Fig.4a. The high uptake at very low pressures (0-0.1 bar) indicates the material was microporous. With increase of pressure, the nitrogen uptake increased slightly, indicating the existence of a little external surface area due to the presence of very small particles. Therefore, **Al-CMP** has a predominantly microporous structure in its framework. The sharp increase in the nitrogen uptake at high relative pressure may be attributed in part to interparticulate porosity associated with the meso- and macrostructures of the sample. A surface area of 839 m² g⁻¹ was obtained by applying the Brunauer-Emmett-Teller (BET) model and a surface area of 1278 m² g⁻¹ was obtained by applying the Langmuir model within the pressure range of $P/P_0 = 0-1$ bar (Table 1). The pore-size distribution diagram based on the density functional theory (DFT) method in Fig.4b also showed a typical microporous nature of the material, and the pore size was estimated as 1.42 nm. According to Table 1, the total pore volume of **Al-CMP** was 2.14 cm³ g⁻¹, which was substantially larger than the volume of many porphyrin-based CMPs, including MPPF-2 (0.61 cm³ g⁻¹),²⁴ CoP-CMP (0.36 cm³ g⁻¹),²⁵ PCPF-1 (0.86 cm³ g⁻¹).²⁶ Metal (Al) was detected in polymer by inductively coupled plasma-optical emission spectroscopy (ICP-

OES). The content of Al in polymer was found to be 2.81 wt%, revealed 1.04 mmol g⁻¹ metal-porphyrin species for **Al-CMP**, which was slightly less than the theoretical value of 3.11 wt%, indicating that a small portion of porphyrin ligands in the **Al-CMP** was not coordinated to metal atoms. Furthermore, **Al-CMP** was stable at a high temperature up to ~ 400 °C, displaying good thermal stability (Fig.4c).

Because of its high surface area and pore volume, abundant

Table 1 Physical properties of **Al-CMP**

Polymer	S_{BET} (m ² g ⁻¹) ^a	S_{Lang} (m ² g ⁻¹)	S_{micro} (m ² g ⁻¹) ^b	V_{tot} (cm ³ g ⁻¹) ^c	V_{micro} (cm ³ g ⁻¹) ^d	M_{calc} (wt%) ^e	M_{ICP} (wt%) ^f	CO ₂ uptake (mg g ⁻¹) ^g
Al-CMP	839	1278	229	2.14	0.103	3.11	2.81	27.43

^a Specific surface area calculated from the nitrogen adsorption isotherm using the BET method. ^b Micropore surface area calculated from the nitrogen adsorption isotherm using the t-pot method. ^c Total pore volume at $P/P_0 = 0.99$. ^d Micropore volume calculated using the t-pot method. ^e Data calculated based on each monomer unit. ^f Data obtained with inductively coupled plasma-optical emission spectroscopy (ICP-OES). ^g Volumetric CO₂ adsorption-desorption isotherms measured for **Al-CMP** at 298 K.

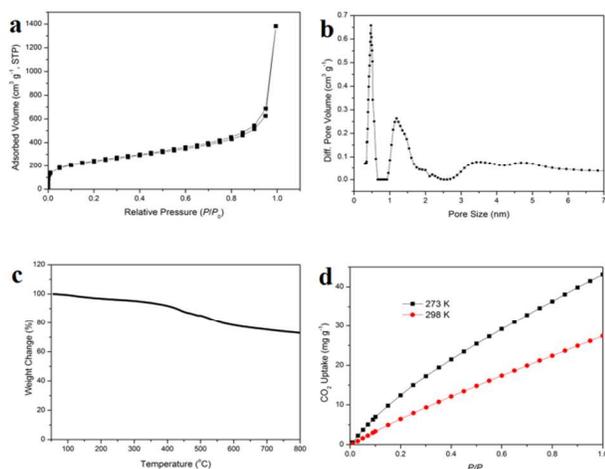


Fig. 4 (a) N₂ adsorption-desorption isotherms of **Al-CMP** (77 K), (b) Pore size distribution diagrams (based on DFT method) of **Al-CMP**, (c) TGA curve of **Al-CMP**, and (d) CO₂ sorption isotherms for **Al-CMP** at 273 and 298K, respectively.

Catalytic performance of **Al-CMP**

Considering the porosity of **Al-CMP** and the existence of metal-porphyrin species, **Al-CMP** was used as a solid catalyst for the coupling of carbon dioxide and propylene oxide (PO). The results were summarized in Table 2.

Generally, a cocatalyst, such as amine, phosphine or quaternary onium salt, played a significant role in the coupling of CO₂ and PO.²⁷ In the absence of any cocatalyst, the coupling reaction by **Al-CMP** yielded only 1.5% PC at 70 °C (Entry 1). Once the cocatalyst was used, the catalytic activity of **Al-CMP** increased notably (Entries 2-5). With PPNCI as cocatalyst, **Al-CMP** exhibited high catalytic activity and 74% PO conversion was obtained at 70 °C and 3 MPa for 5 h, while PO conversion was low (27%) with PPNCI alone (Entry 11). In addition, no other by-products were observed in the conversion to propylene carbonate (PC) by **Al-CMP**. When PPNCI was replaced by TBAB, the catalyst system gave a relatively low catalytic activity and the PO conversion was only 28%. When amines (DMAP, MeIm) were employed as cocatalysts, the PO conversions decreased significantly to below 10%. Therefore, PPNCI was the best cocatalyst in this catalyst system. Furthermore, the molar

nitrogen atoms and coordinated metal sites, **Al-CMP** exhibited a good CO₂ uptake capacity as shown in Fig.4d. When the pressure P (actual pressure) approached 760 mm Hg (that is, P/P_0 approached 1), the CO₂ uptake reached 27.43 mg g⁻¹ at 298 K and 43.12 mg g⁻¹ at 273 K. Its adsorption curves gradually increased with increasing pressure, suggesting further high adsorption capacity for carbon dioxide at elevated pressure.

ratio of catalyst (**Al-CMP**) to co-catalyst (PPNCI) was also a major factor for the catalytic activity (Entries 2 and 6). When the molar ratio of **Al-CMP** to PPNCI was changed from 1:10 to 1:1, the PO conversion decreased from 74% to 22%.

As observed, temperature also had a strong influence on the catalytic activity. As shown in Table 2, a rise of temperature from 25 to 100 °C favored PO conversion. At 25 °C, PO conversion was only 3%. With temperature raising, PO conversion increased exponentially, and reached to 91% at 100 °C. Generally, CO₂ pressure was also a major factor on coupling of CO₂ and PO. However, when CO₂ pressure decreased from 3 to 1 MPa, the PO conversion varied insignificantly, indicating that the rate of coupling reaction was almost independent of CO₂ pressure in this range.

Table 2 Coupling reaction of CO₂ and PO catalyzed by **Al-CMP**^a

Entry	Cocatalyst	Temperature (°C)	Pressure (MPa)	Conversion (%) ^b	TON ^c	TOF (h ⁻¹) ^d
1	--	70	3	1.5	30	6
2	PPNCI	70	3	74	1480	296
3	TBAB	70	3	28	560	112
4	DMAP	70	3	6.1	122	24
5	MeIm	70	3	9.2	180	37
6 ^e	PPNCI	70	3	22 ^f	440	55
7	PPNCI	25	3	3.0	60	12
8	PPNCI	50	3	43	860	172
9	PPNCI	100	3	91	1820	364
10	PPNCI	70	1	73	1460	292
11 ^g	PPNCI	70	3	27	540	--

^a Reaction conditions: PO (10 mL), [PO]/[Al]/cocatalyst = 2000:1:10, 5 h. ^b Determined by ¹H NMR spectroscopy. ^c Turnover number of PO to products. ^d Turnover frequency of PO to products. ^e Reaction conditions: PO (10 mL), [PO]/[Al]/cocatalyst = 2000:1:1, 8 h. ^f Polycarbonates (4.6%) were observed by ¹H NMR spectroscopy. ^g Reaction conditions: PO (10 mL), [PO]/[PPNCI] = 2000:10, 5 h.

Recently, metallosalen-based CMPs have been used as solid catalytic systems to catalyze the coupling of PO and CO₂.¹⁸ These solid systems showed TOFs of 109-224 h⁻¹ at 100 °C^{18a, 18b} and 40-157 h⁻¹ at 60 °C.^{18c} By contrast, **AI-CMP** in this work showed TOFs up to 364 h⁻¹ at 100 °C and 296 h⁻¹ at 70 °C, which indicated this metalloporphyrin-based CMP was an efficient solid catalyst for CO₂ conversion to cyclic carbonates.

An important additional feature for any catalyst having potential practicability is its reusability without significant loss in catalytic activity. As shown in Fig. 5, the catalyst was recycled for five runs under the same reaction conditions (70 °C, 3 MPa, 5 h). Following each cycle, **AI-CMP** was simply recovered by filtration after reaction and reused for next run after being dried. The PO conversion and TOF gradually decreased with increase of reused times, but they still kept above 50% and 200 h⁻¹ after 5 runs respectively. The aluminum content in **AI-CMP** after 5 runs was determined to be 0.78 wt% by ICP-OES, which was much lower than the original value (2.81 wt%). This indicated that the metal aluminum was partially dissociated from the porphyrin ligand of **AI-CMP** during the reaction and dissolved in the reaction system, which may be the main reason for the decrease in catalytic activity.

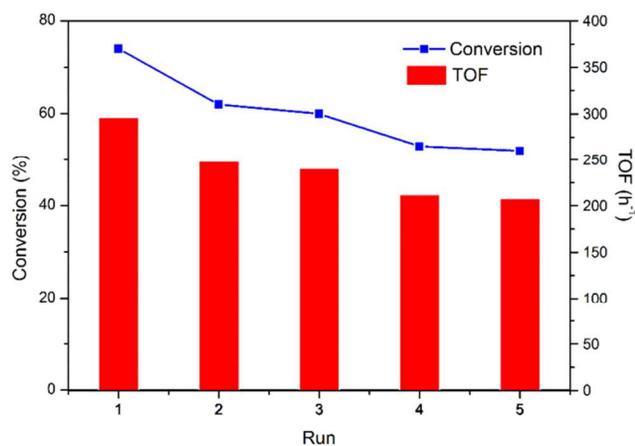


Fig. 2 Recycle experiment with **AI-CMP**. Standard reaction conditions: 0.05 mol% **AI-CMP**, 0.5 mol% PPNCI, 70 °C, 3 MPa, 5h.

Conclusions

A new metalloporphyrin-based conjugated microporous polymer (**AI-CMP**) was solvothermally synthesized using a metalloporphyrin as a main building block, which had high BET surface area and good capacity of carbon dioxide capture. When PPNCI was used as co-catalyst, **AI-CMP** displayed good catalytic activity for cyclic carbonate synthesis with 364 h⁻¹ TOF. Furthermore, **AI-CMP** had relatively good stability, and the PO conversion and TOF still kept above 50% and 200 h⁻¹ respectively after it was reused 5 times.

Acknowledgements

The authors thank financial support from the National Natural Science Foundation of China (Grant No. 51321062, 51273197 and 21134002).

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