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Increasing mesoporosity by a silica hard template in a covalent organic polymer for enhanced amine loading and CO_2 capture capacity

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ABSTRACT

Solid sorbents for chemisorptive carbon dioxide uptake in post-combustion scenarios require strong binding groups like amines. Post-synthetic impregnation of reactive amines requires large pore volumes. Covalent organic polymers (COPs) are microporous (or narrow mesoporosity) network polymers with physisorptive behavior. Herein as the first of such attempt in porous organic polymers, we modified COP-1, which is an inexpensive, scalable porous polymer for effective amine loading. By expanding the pore of COP-1 through hard templation by silica, the surface area and pore volume are increased by 2.3 and 2.9 times, respectively. It was shown that the increase of pore volume was mostly from pores larger than 5 nm and it correlates well with the silica particle size (12 nm) and the inter-particle pore sizes of silica (31 nm). As a result, amine impregnated Si-COP-1 adsorbs CO_2 with the increase of 2.44 at 273 K and 4.06 times at 298 K (at flue gas relevant partial pressure of 0.15 bar) over the parent COP-1. Our results show the possibility of tuning porosity for developing industrially feasible CO_2 capturing sorbents.

1. Introduction

Carbon Capture and Storage (CCS) has received significant attention as carbon dioxide (CO_2) concentration in atmosphere has reached hazardous limits. A CCS project consists of three main parts: capture, transport and storage. Among them, the capture is the key technology to initiate storage of CO_2 under the ground or convert it to beneficial products. The power plants are the main CO_2 emission sources with 3 different modes of CO_2 capture potential: post-, pre- and oxyfuel-combustion processes. Post-combustion has been considered the most applicable process because of the simpler implementation, e.g. retrofitting conventional, existing plants. The flue gas contains 15% of CO_2, 3.5% of water vapor, and remainder being N_2 with little amount of SO_x, and NO_x [1]. Thus CO_2 selectivity to N_2 is the most important feature in a capture process. The operation temperature is around 40–60 °C with ambient pressure.

Wet scrubbing technologies using amine solutions are widely used in industrial CO_2 separations. Aqueous monoethanolamine (MEA) with high chemisorptive CO_2 selectivity over other gases is the standard sorbent, even though it requires excessive regeneration energy due to the chemical bond between CO_2 and amine by zwitterion mechanisms, as well as the high heat capacity of water [2]. Thus, an energy penalty of 25–40% by MEA solutions is a severe drawback. The water which comprise amine solution also causes corrosion, another undesired down time for the scrubbers [3]. It is, therefore, evident that moderately chemisorptive solid sorbents would solve many of these issues.

Physical adsorbents that require less energy for regeneration are studied as alternatives such as activated carbons, zeolites and metal organic frameworks (MOFs) [4]. Microporosity of physisorbents is the significant feature for adsorbing CO_2 through van der Waals forces between adsorbent and adsorbate [5–8]. But their selectivity is too low to commercialize them in plant scale. The disadvantages led researchers to utilize both chemical and physical characteristics in adsorptive uptake of carbon dioxide [9,10].

Amine impregnation is one of the simplest methods among various amine modifications for combination of chemisorption and physisorption [11–16]. Micropores (pores < 2 nm) are too small and get clogged by the incoming amine molecules. The adequate property for efficient amine impregnation would be a mesoporous (2 nm $<$ pores $<$ 50 nm) material with large pore volume [17].

Several researchers had controlled the porosity for synthesizing porous materials with specific pore size. R. Banerjee et al.

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synthesized ZIFs having different pore size by adjusting each functional groups [18]. E. Prouzet et al. changed reaction temperature for control of pore in mesoporous molecular sieves developed through nonionic surfactant [19]. R. Ryoo et al. synthesized ordered carbon materials by MCM-48 and SBA-15 as the template [20,21]. T. Yildirim et al. has made high pore volume materials by carbonizing MOF-5 into hierarchically porous carbons (HPCs) before loading with amines to get high CO_2 uptake [17]. There are two different kinds of templates for inducing porosity: soft and hard templates. Organic compounds such as block copolymers are used as soft template with some difficulty in removing from one organic phase from the other. Hard templates from inorganic matter such as MCM-48, and SBA-15, on the other hand, would be easily removed if organic porous network were intended.

In this work, we studied a covalent organic polymer (COP-1) as a platform to tune porosity for efficient amine loading and enhanced CO_2 uptake. COP-1 has narrow average pore size ($\leq$4 nm), which brings high selectivity to CO_2 [22] but weak binding due to the physisorptive nature of interactions. First, we expanded pore size distribution of COP-1 by hard templating with silica nanoparticles due to their high stability, ease of removal, and commercial availability in nano sizes. We show a systematic increase in mesoporosity of a physisorptive COP-1 structure that is more suitable for amine impregnation. Our results with amine impregnation in pore-expanded structure indicate twice (273 K) and four times (298 K) increase in CO_2 capture at flue gas partial pressure of 0.15 bar.

2. Experiments

2.1. Materials

Cyanuric chloride (CC, 98%), piperazine (PZ, 98%, anhydrous), triethylenetetramine (TETA, 60%), and pentaethylenehexamine (PEHA) were purchased from Tokyo Chemical Industry (TCI) from Japan. Polyethylenimine (PEI, MW = 300), N, N−diisopropylethylamine (DIPEA, 98%) and silica nanoparticle (SiO_2, 12 nm) were purchased from Sigma-Aldrich, USA. Sodium hydroxide (NaOH, bead, 98%), 1, 4-Dioxane (98%), ethyl alcohol, and methyl alcohol were purchased from SAMCHUN, South Korea. All solvents were dried and stored in anhydrous conditions before utilization in the synthesis.

2.2. Synthesis

2.2.1. Synthesis of SiCOP-1

SiO_2 (3.26 g, 54.2 mmol) was dried at 150 °C under vacuum for 3 h. After cooling down it to room temperature under inert atmosphere, 1, 4-dioxane (70 mL) was injected with constant stirring. DIPEA (18.9 mL, 108.4 mmol) was added to the solution at 15 °C. CC (5 g, 27.1 mmol) which dissolved in 1, 4-dioxane (50 mL) was added dropwise. PZ (3.73 g, 43.4 mmol) which dissolved in 1, 4-dioxane (100 mL) was added as keeping temperature at 15 °C. The reaction continued at 15, 25 and 85 °C on 1, 2, and 21 h, respectively. The beige precipitate was filtered with dioxane. For etching silica template, NaOH solution (1 M, 500 ml) was mixed with the precipitate at 90 °C for 6 h and then filtered out using distilled water. The etch step was done two times. Finally, the precipitate washed with 1, 4-dioxane, water and ethanol was dried at 110 °C under vacuum for 6 h [23].

2.2.2. Synthesis of amine impregnated COP-1 and SiCOP-1

COP-1 was first successfully reproduced from the reference [22]. TETA (0.5 g) dispersed in methanol (5 mL) was added in the solution of COP-1 or SiCOP-1 (0.5 g), and methanol (5 mL). The mixture was stirred at room temperature for a day. The precipitate obtained by centrifuge (7500 rpm, 5 °C) was dried in oven at 100 °C under vacuum for 6 h. Same sequences were repeated in case of PEHA and PEI impregnation. Amine impregnated samples in COP-1 or SiCOP-1 were designated with the order of kinds of COP, amine, the weight ratio of amine over COP. For example, COP-1-TETA100 is 100 wt % of TETA was impregnated inside of COP-1. SiCOP-1-TETA100 means same kind and amounts of amine was impregnated in SiCOP-1.

2.3. Characterization

Elemental analysis of all samples for C, H, N and S was measured by FLASH 2000 series (Thermo Scientific, USA) with accuracy of 0.3%. Flash EA 1112 (Thermo Finnigan, Italy) was used for measuring oxygen with same accuracy. The morphology was measured by Field emission scanning electron microscope, Nova230, (FEI Company, USA). Thermogravimetric analysis (TGA) were carried out on a SHIMADZU-TG 60A under N_2 or air atmosphere by heating samples to 800 °C at the rate of 10 °C min^{-1}. The functional groups of polymer were checked thorough FT-IR spectra using KBr pellets by a Perkin-Elmer FTIR spectrometer. N_2 sorption isotherms at 77 K were obtained with a Micromeritics 3Flex surface characterization analyzer. The adsorption-desorption isotherms of CO_2, N_2, CH_4, and H_2 were also measured by 3Flex. Before sorption measurement, samples without amine were degassed at 150 °C for 5 h under vacuum, and with amine at 100 °C.

3. Results and discussion

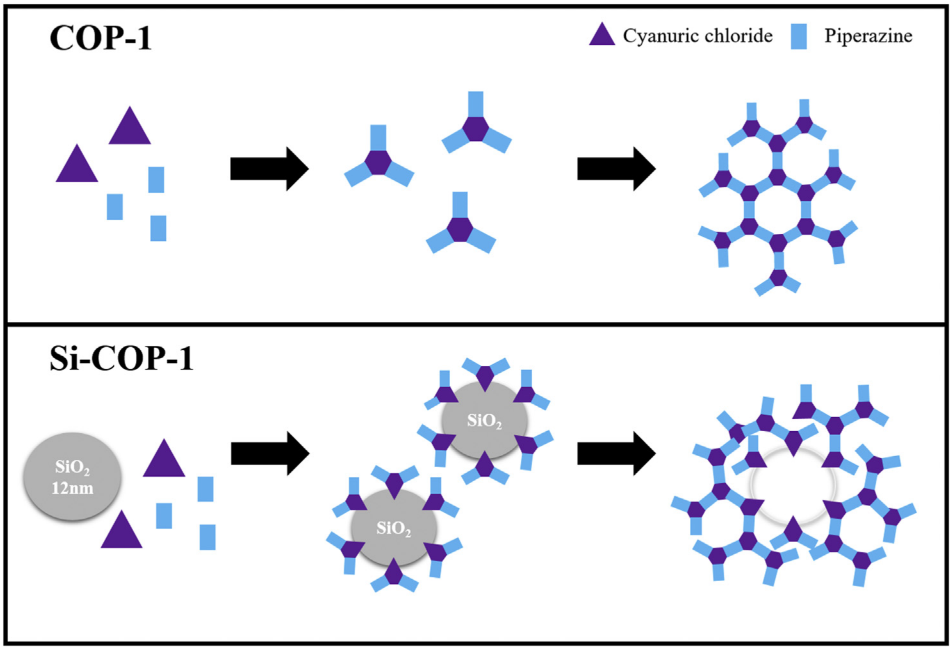
Original COP-1 is a physisorptive sorbent with reasonably high selectivity to CO_2 over N_2 due to the available nitrogens in its structure; however, CO_2 uptake capacity is still low [22]. Amines, known for their reactivity towards CO_2, have been studied for impregnation in adsorbents, which can increase CO_2 uptake especially in the low partial pressure range by chemisorption [24–26]. For the effective amine impregnation, large volume, which is often found in mesopores, is critical. Micropores, on the other hand, would be blocked by amines, which limits the diffusivity of CO_2. Macropores (pores > 50 nm) are too large to retain amines inside. In order to increase mesoporosity in our materials, we chose hard templation methods. In hard templation, porous network is created around sacrificial inorganic solids that have grain sizes similar to the desired pore size. After the hard template is dissolved, new porosity or order is generated (Scheme 1).

3.1. Change in porosity by silica hard template

3.1.1. Structure characterization

In COP-1 synthesis (Fig. 1), dioxane dispersion of CC was added dropwise to the solution of PZ and DIPEA in dioxane, whereas in case of silica template for COP-1 we reacted dried silica with CC first in the presence of base (DIPEA) and introduced PZ for networks formation (Scheme 1). CC was introduced first to the silica in order to start growth on silica surface. For an optimum order, other control experiments were conducted with different sequences. (Scheme S1). In most of template synthesis, surface area or pore volume increased relative to COP-1 except PZ put first (Table S1). SiCOP-1-1 is selected for the highest pore volume and surface area (Fig. S1).

To optimize silica amount, four different silica/CC (mol) experiments were conducted. The ratio is represented as X of SiCOP-1-X and X is 0.5,1,2, and 4. SiCOP-1-0.5 shows the highest pore volume but the case of SiCOP-1-2 has the highest surface area and CO_2 uptake with less than 0.01 decrease in pore volume (Table S1, Fig. S2).



Scheme 1. Procedure for increasing mesoporosity of COP-1 by hard templation.

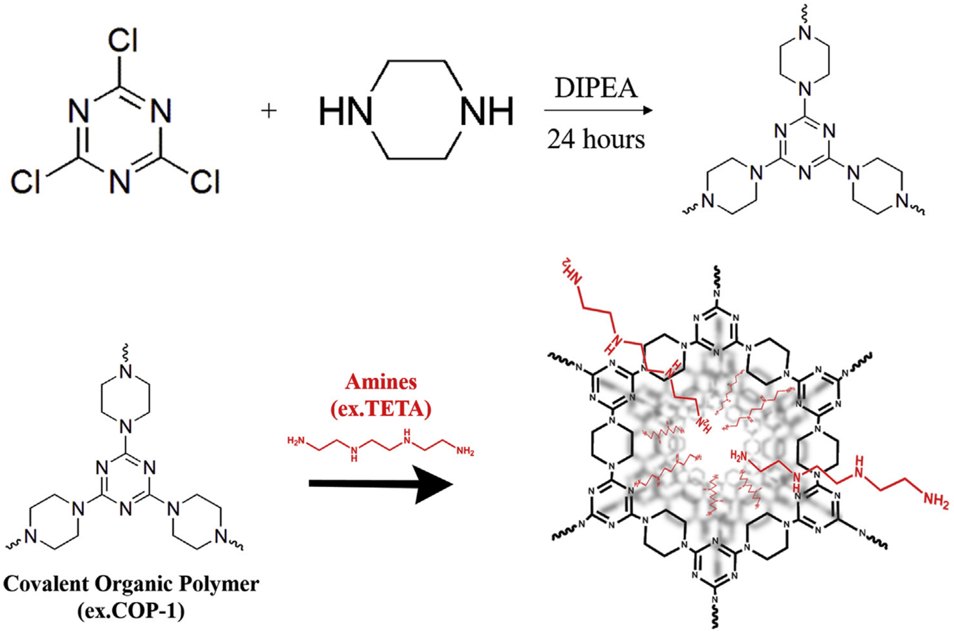


Fig. 1. Easy synthesis and illustrative description of amine impregnation of Covalent Organic Polymer (COP)-1.

Almost all structures we worked on have two peak groups around 32 nm (similar with silica template's interstitial pores) and the original COP-1 peak at 4 nm (Fig. 2). For accurate comparison, we synthesized all of them in ten times larger scale from the original COP-1 procedure. Templated samples have an enhanced ~30 nm peak induced by silica hard template but especially evident with the sharp increase in the silica particle size range of 5–20 nm (Fig. S3). The results indicate that moderate silica amount leads to increasing instances of reaction around them but chances decreased when too many particles are aggregated on each other.

In Table 1, the effect of silica template can be estimated by comparing the elemental ratio of carbon and hydrogen over nitrogen between theoretical COP-1 and experimental COPs. Nitrogen could only come from monomers and setting nitrogen as a reference point is more reasonable than other components. There could be several reasons for higher values in C/N and H/N than theoretical, but we suspect the values come mainly from left over piperazine terminals. The difference of SiCOP-1 is relatively higher than that of COP-1. It is because CC arms also left alone after silica was etched away. One of the three arms of C–Cl bonds in CC, which reacts with –OH of silica surface, remains with –OH. Amine impregnated samples have clear difference in H/N ratio (0.32) since it contains a lot of TETA, which is 2.2 times higher than the theoretical COP-1.

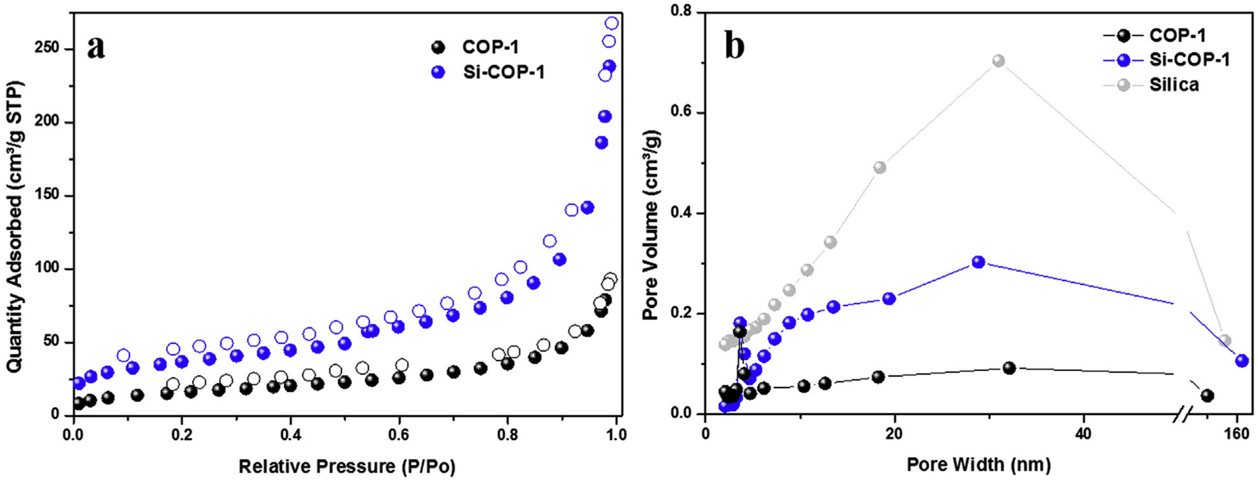


Fig. 2. Tuning COP-1's porosity: (a) N_2 adsorption-desorption isotherm @ 77 K of COP-1 and silica templated COP-1 (SiCOP-1), (b) their pore size distribution by BJH method.

Table 1
Elemental analysis of COP-1, SiCOP-1 and their amine impregnated samples.

Samples	N(%)	C(%)	H(%)	O(%)	C/N	H/N
Theoretical COP-1	41.15	52.93	5.92	–	1.29	0.144
COP-1	33.38	44.01	4.85	1.29	1.32	0.145
COP-1-TETA100	34.74	45.61	6.17	1.74	1.31	0.178
SiCOP-1	34.32	47.28	5.73	2.68	1.38	0.167
SiCOP-1-TETA100	34.04	48.53	6.62	3.65	1.43	0.194

Fig. 3a shows the characterization of structures for their functional groups. COP-1 and SiCOP-1 do not have C—Cl peak around 540–785 cm^{-1} indicating that all arms in CC were reacted. A control sample before etching silica away (SiCOP-1-BE) was also measured and there is only a different new peak around 1200–1016 cm^{-1}, which is a characteristic stretching of a Si—O bond. The fact that no Si—O peak in SiCOP-1 left over proves that etching was successful.

Thermogravimetric analysis (TGA) graph in air (Fig. 3b) also confirms that silica is completely etched. SiCOP-1 became 0% from 670 °C on but SiCOP-1-BE had 34.12% left even above 700 °C, most likely due to the highly stable SiO_2. The first weight loss step is before 100 °C where water and solvents usually leave. After that, new structures decomposed with similar profiles of COP-1.

3.1.2. *Porosity*

The surface area which was calculated with BET model of COP-1 was 57.77 m^2/g, a lower value than our earlier work [22] and we suspect the purity effects of solvents, reactivity loss due to the order of addition and user errors. In amorphous constructs, this is likely to happen as the random polymerization of the struts do not confer perfectly each time. Pore size distribution was calculated by BJH theory since it provides good fit in especially mesoporous regions [27]. SiCOP-1 had 2.28 and 2.92 times higher in surface area and pore volume than COP-1 (Table 2). Initial pore volumes until 4 nm peak are almost same but SiCOP-1 has much higher value above 5 nm up to 160 nm (Fig. 2). Also, it has another new peak around 28 nm, which is now a dominant pore. The increased pore volume was generated obviously from silica particles. The SEM image of

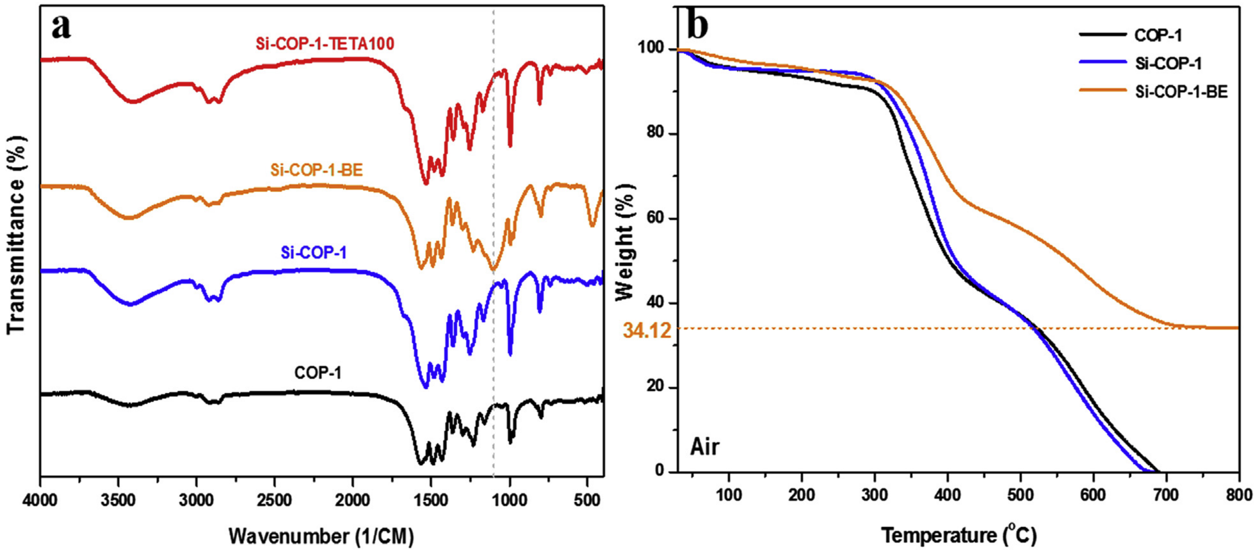


Fig. 3. Characterization of COP-1, SiCOP-1 and their amine impregnated derivatives: (a) FT-IR spectra of COP-1(black), SiCOP-1(blue), SiCOP-1 before silica etching(orange), and amine impregnated SiCOP-1(red). (b) TGA spectra in air atmosphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Porosity and selectivity of COP-1, SiCOP-1 and their amine impregnated samples.

Samples	S_{BET}[a] (m^2/g)	S_{micro}[b] (m^2/g)	V_{BJH}[c] (cm^3/g)	CO_2 uptake(mg/g) @ 0.15 bar	
				273 K	298 K
COP-1	57.77	3.281	0.1317	18.92	8.12
COP-1-TETA100	27.31	5.431	0.0920	27.45	17.61
SiCOP-1	131.8	29.70	0.3848	26.88	12.76
SiCOP-1-TETA100	74.12	4.56	0.3528	46.18	32.97

[a] Surface area calculated with BET theory.
[b] Surface area in microporous region calculated by t-plot method.
[c] Total pore volume estimated by BJH desorption isotherm.

SiCOP-1-BE shows the structure of silica-COP-1 composites (Fig. 4). The grain morphologies of COP-1 before and after templation display similar textural properties, confirming an intrinsic templation. There are, however, other sites of interest for expanding pore size distribution. For example some contributions may come from inter-particle voids that are formed by template directed crosslinking.

3.2. Increasing CO_2 affinity by amine impregnation

Different types of amine such as TETA, PEHA, and PEI were impregnated in COP-1, and SiCOP-1 (Table S1, Fig. S4) in order to develop an effective CO_2 sorbent. All of the impregnated samples had losses in surface areas and pore volumes with increased CO_2 uptake ability especially at low-pressure region, leading to our conviction that the impregnation was successful (Fig. 5). Also, CO_2 uptake have significantly improved on SiCOP-1 (more so than COP-1) even though the loading dose of amines were similar for all. Among different kinds of amine, TETA is the most effective amine showing the highest increased affinity towards CO_2.

Various amounts of TETA were therefore impregnated to find an optimum ratio. The more amine was impregnated, the more surface area and pore volume were decreased (Table S1). SiCOP-1 with 100% (w/w) impregnated amine ratio shows the best CO_2 uptake of especially in the low-pressure range (Fig. 5 and S5). Its CO_2 capacity at 273 K and 298 K (0.15 bar) is 1.72 and 2.58 times higher over SiCOP-1, whereas 1.45 and 1.89 times in case of COP-1 and COP-1-TETA100, respectively. Although the amount of impregnated amine is same, samples based on the SiCOP-1 always shows higher increase. SiCOP-1-TETA100 adsorbs CO_2 at very low pressures, which is evident for chemisorptive behavior. COP-1 and SiCOP-1, on the other hand, shows slowly increase because of their physisorptive nature. This is also shown in the selectivity of CO_2 over other gases since it became higher with amine impregnation. The CO_2 selectivity of SiCOP-1-TETA100 is 936 over N_2 (post-combustion condition, $CO_2/N_2 = 15/85$) at 273 K, whereas those of COP-1 and SiCOP-1 are 55 (Fig. 5). The 17 times increased selectivity to CO_2 also leads to rising heat of adsorption into the desirable range of 30–50 kJ/mol. This high selectivity offers another desirable property for the templation methodologies.

To know impregnated amount of TETA, thermal analysis in the nitrogen atmosphere was conducted (Fig. 6a). All of samples were degassed at 80 °C for 1 h to get rid of the effect of remained solvent, moisture and gas. SiCOP-1 starting to decompose from as early as 250 °C with the inflection point at 525 °C, whereas its amine impregnated samples collapsed even earlier with similar trends of pure TETA. The more amine were impregnated inside COPs, the

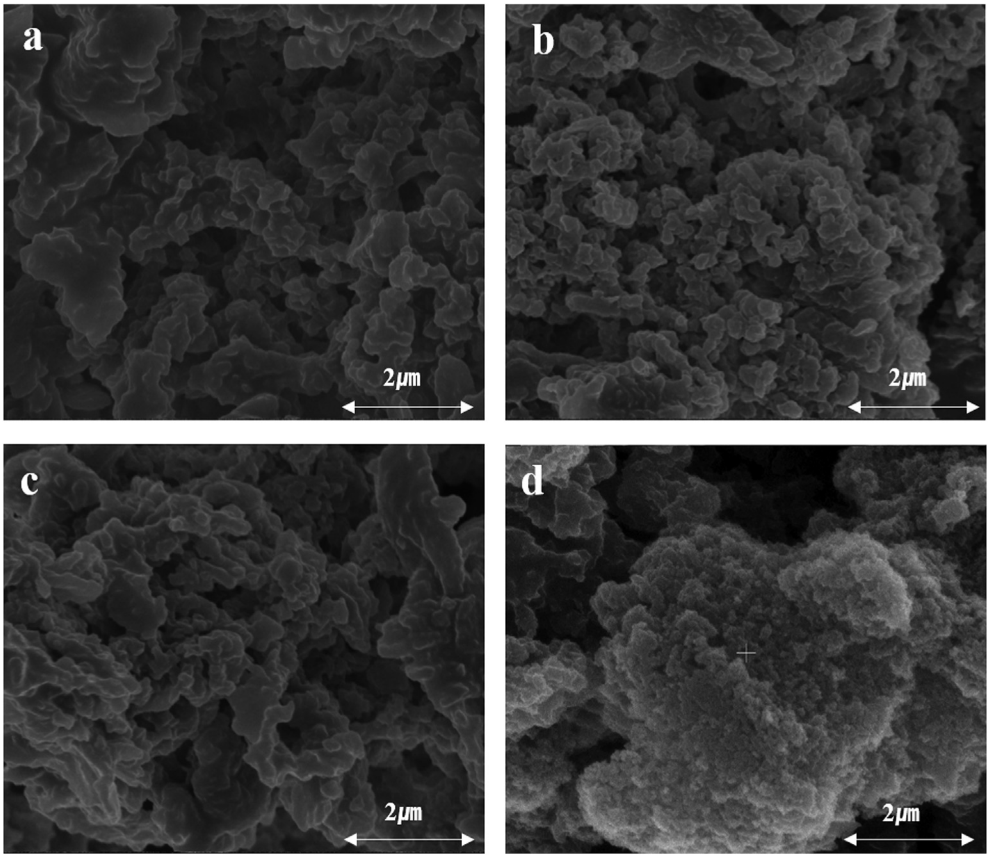


Fig. 4. SEM images of (a) COP-1, (b) SiCOP-1, (c) SiCOP-1-TETA100 (TriEthylene TetraAmine), and (d) SiCOP-1-BE (Before Etching).

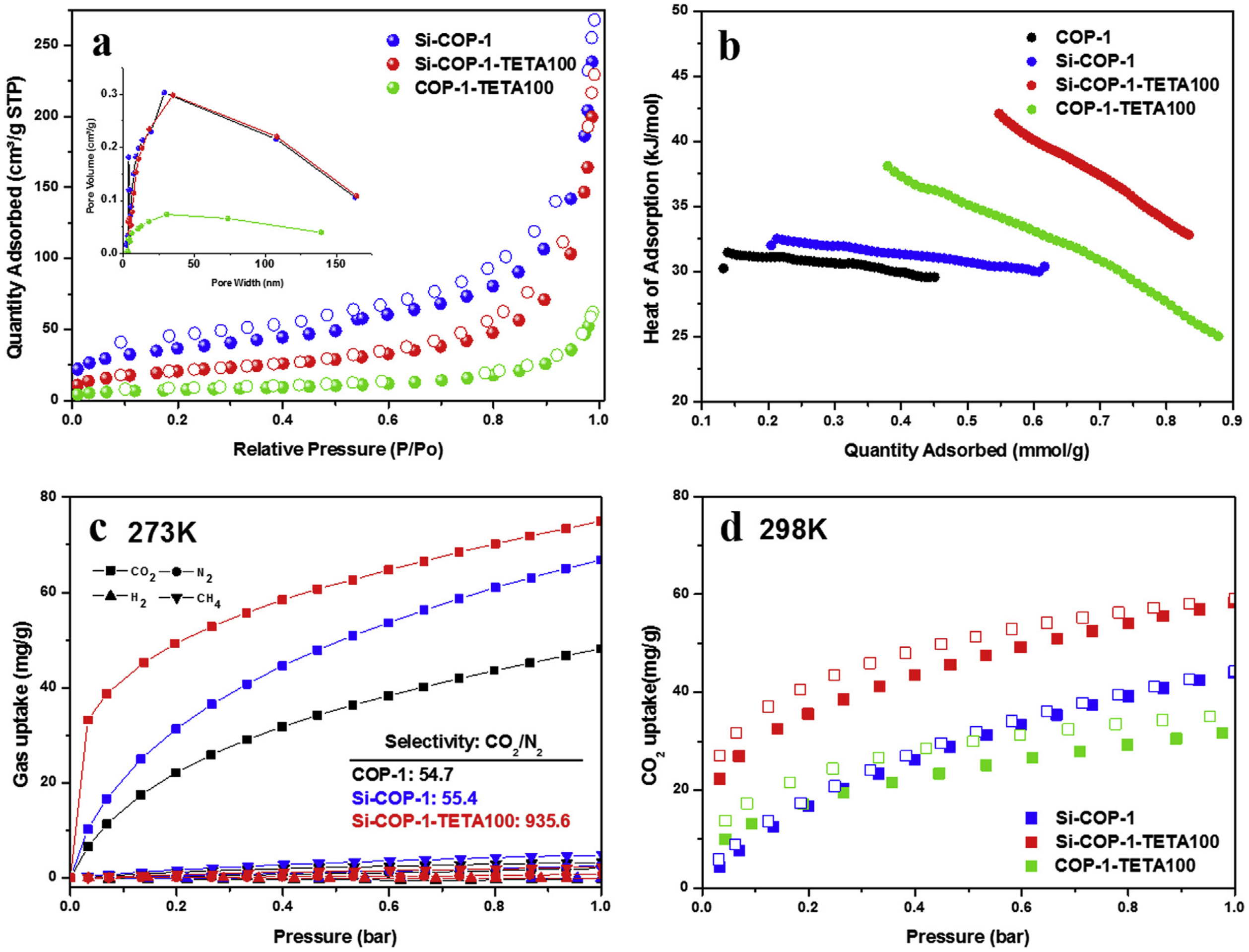


Fig. 5. Gas uptake capacities and characteristics of amine (TETA) loaded COP-1 and derivatives: (a) BET surface areas and pore size distributions (inset) based on BJH theories, (b) Heat of adsorption for CO_2 uptake in the sorbents, (c) Gas (CO_2, N_2, H_2, CH_4) uptake capacities in 273 K and (d) CO_2 uptake in 298 K.

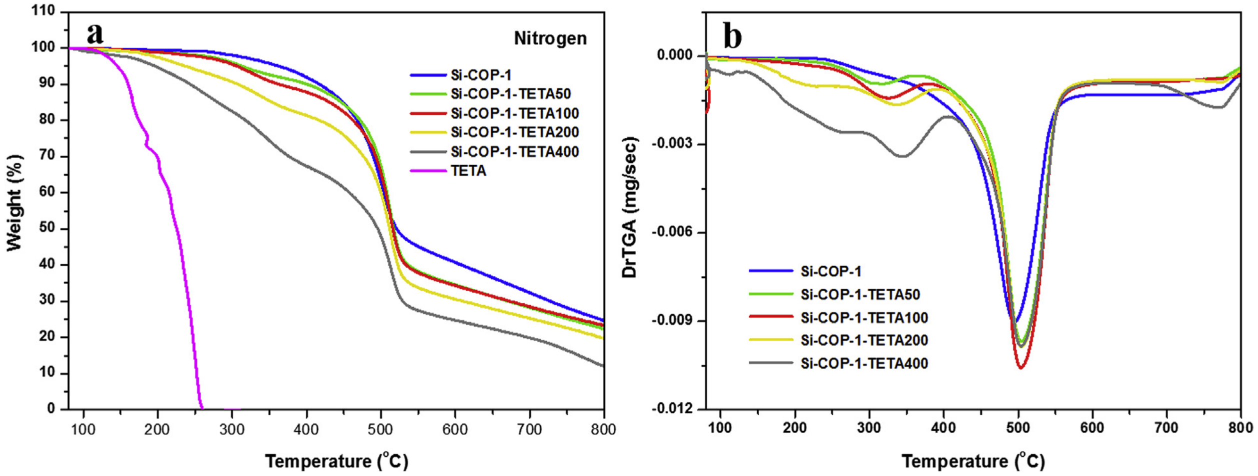


Fig. 6. (a) TGA of COP-1, SiCOP-1 and their amine impregnated samples in N_2 atmosphere (b) Differential TGA graph of (a).

more weight (%) were decreased and the earlier decomposition started. With the help of differential thermogravimetric curve in Fig. 6b, we could calculate that there is 6.6% of amine in SiCOP-1-TETA100. Thermal studies also indicate that amine impregnated mesoporous COP-1 can be used as a sorbent in CO_2 capture from flue gas.

4. Conclusions

In summary, the porosity of COP-1 was tuned to increase pore volume, in order to load reactive amines for an enhanced CO_2 capture. The silica templated covalent organic polymer, SiCOP-1, shows well defined mesoporosity, relevant to the properties of the silica template. As a result, CO_2 uptake capacities increased up to four times. With the controlled pore, the characteristics of pore can be improved by impregnation with various guests for different kinds of applications such as gas separation and storage, catalyst, drug delivery and so on. In addition, this study can be applied to other organic porous polymers for controlling surface area, pore volume and pore size distribution.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2016.04.019.

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