



# Preparation of microporous polyamide networks for carbon dioxide capture and nanofiltration

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## ARTICLE INFO

### Article history:

Received 13 September 2012

Received in revised form

26 November 2012

Accepted 1 December 2012

Available online 6 December 2012

### Keywords:

Microporous polyamides  
Interfacial polymerization  
Nanofiltration

## ABSTRACT

For the first time, microporous polyamide networks have been synthesized via the interfacial polymerization of piperazine and acyl chloride monomers containing tetrahedral carbon and silicon cores. These polyamides, with Brunauer–Emmett–Teller surface area between 488 and 584 m<sup>2</sup> g<sup>-1</sup>, show a CO<sub>2</sub> uptake of up to 9.81 wt% and a CO<sub>2</sub>/N<sub>2</sub> selectivity of up to 51 at 1 bar and 273 K, suggesting their great potential in the area of carbon capture and storage applications. We have developed the interfacial polymerization on the surface of the porous polyacrylonitrile substrate, resulting in the formation of ultrathin microporous membranes with thicknesses of about 100 nm. These nanofiltration (NF) membranes exhibited an attractive water flux of 82.8 L m<sup>-2</sup> h<sup>-1</sup> at 0.4 MPa and a high CaCl<sub>2</sub> (500 mg/L) rejection of 93.3%. These NF membranes follow the salt rejection sequence of CaCl<sub>2</sub> > NaCl > Na<sub>2</sub>SO<sub>4</sub>, demonstrating the positively charged character of these membranes.

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## 1. Introduction

Microporous organic polymers (MOPs), which contain interconnected pore sizes of less than 2 nm and high specific surface area [1,2], have created significant interest in the field of molecular separation [3], heterogeneous catalysis [4], light harvesting [5], and gas storage [6]. Classes of reported MOPs include covalent organic frameworks (COFs) [7], conjugated microporous polymers (CMPs) [8], hyper-cross-linked polymers (HCPs) [9], and polymers of intrinsic microporosity (PIMs) [10–12]. These microporous materials possessing a high surface area, low skeleton density, and chemical tunability have shown the potential for their application in the area of CO<sub>2</sub> capture [13]. Carbon Capture and Storage (CCS) is becoming increasingly important as the continuous emission of CO<sub>2</sub> to the atmosphere results in global warming [14]. High CO<sub>2</sub> adsorption capacity and its selectivity over N<sub>2</sub> in realistic flue gas emissions are essential in the case of post-combustion carbon capture [15]. It has been reported that the increase of surface area and pore volume is not the only way to increase CO<sub>2</sub> uptake and CO<sub>2</sub>/N<sub>2</sub> selectivity at ambient pressure [16], postsynthetic modification and introduction of functional groups has greater potential to increase CO<sub>2</sub> capacity and selectivity [13]. For example, a porous

polymer network grafted with sulfonic acid and lithium sulfonate showed a significant increase in CO<sub>2</sub> capacity and CO<sub>2</sub>/N<sub>2</sub> selectivity under ambient conditions, in spite of a sharp decrease in the surface area upon functionalization [17].

MOPs are often synthesized by the polymerization of rigid organic molecules with multiple reactive functional groups extending into two or three dimensions. The permanent porosity derives from backbone rigidity and space-inefficient packing of the polymer chains [11]. The methodologies for preparing MOPs at present include Pd(II)/Cu(I)-catalyzed Sonogashira-Hagihara crosscoupling [8], Ni(0)-catalyzed Yamamoto homocoupling [18], Palladium-catalyzed Suzuki coupling [19], and Co(0)-catalyzed trimerization of aromatic alkynes [20], etc. However, one potential limitation of the above synthetic methods is the cost of the metal catalysts. Interfacial polymerization is a rapid, irreversible polycondensation process at the interface between water containing one multifunctional monomer and an inert immiscible organic solvent containing a multifunctional intermediate, resulting in the formation of high-molecular-weight polymers at room temperature within a few minutes [21]. This simple method has been applied to the preparation of polyamides, polyureas, polyurethanes, polyesters, and polycarbonates [22]. To the best of our knowledge, the preparation of microporous polymers via interfacial polymerization has not been reported.

Recently, tetraphenylmethane (TPM) and tetraphenylsilane (TPS) have emerged as attractive moieties for the construction of microporous materials [19,23–28], as these tetrahedral building

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blocks provide widely open and interconnected pores which prevent dense packing of the chains. For instance Ben et al. have described a “state-of-the-art” material, porous aromatic framework (PAF-1), synthesized via a Yamamoto homocoupling of tetrakis(4-bromophenyl)methane, which shows remarkable Brunauer–Emmett–Teller (BET) surface area up to  $5640 \text{ m}^2 \text{ g}^{-1}$  [24]. Furthermore, the BET surface area can be enhanced to  $6461 \text{ m}^2 \text{ g}^{-1}$  by replacing the central carbon with silicon [28], which is currently the highest surface area reported for purely organic porous materials. However, the processability of microporous organic networks into membranes or films is often difficult as they are mostly insoluble in common organic solvents [29]. Polymer-based microporous membranes are more attractive than insoluble powders for they combine the microporosity and processability of polymers [30]. Membrane technology is widely used in industrial manufacturing as it saves resources, is environment friendly and has a clean production process. Budd, Mckeown and co-workers have explored soluble and linear PIMs that can be processed readily using solvent-based techniques to form membranes [10]. Besides, there are reports of other types of polymer-based microporous membranes or films, such as thermally rearranged polymer membranes [31], fully aromatic hyperbranched polyester films [25], and triazine-framework-based porous membranes [32]. More recently, sol–gel-processable microporous organic networks have been synthesized by urea-forming condensation reaction [33]. The networks obtained through condensation of tetrakis(4-aminophenyl)methane and linear hexamethylene diisocyanate exhibited surface areas in the range of  $188\text{--}551 \text{ m}^2 \text{ g}^{-1}$  ( $\text{CO}_2$  as adsorption gas) and free-standing films can be produced by depositing the organic sols and then evaporating the solvent. But the gelation time of the reaction was about 85 h, which might be inconvenient for practical applications. Herein we present the preparation and characterization of microporous polyamide networks by interfacial polymerization for the first time. By introducing rigid TPM and TPS moieties to the networks, the polyamides show excellent  $\text{CO}_2$  capacity and  $\text{CO}_2/\text{N}_2$  selectivity. We have also developed the interfacial polymerization on the surface of porous polyacrylonitrile (PAN) substrate, resulting in the formation of microporous nanofiltration (NF) membranes. The performance of these microporous membranes for the decontamination of water have also been investigated in this work.

## 2. Experimental section

### 2.1. Materials

Chlorotriphenylmethane, 4-bromotoluene and tetra-chlorosilane were purchased from J&K and used as received. 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), piperazine (PIP) and palladium acetate were obtained from Alfa Aesar. High purity carbon monoxide (99.99%) was obtained from Dalian Airchem Specialty Gases & Chemicals Co., Ltd. High purity nitrogen (99.999%) and carbon dioxide (99.999%) were obtained from Changchun Juyang Gas, Co., Ltd. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/potassium alloy with benzophenone in nitrogen atmosphere. All other solvents and reagents were in chemically pure grade and used as purchased unless otherwise noted.

### 2.2. Preparation of polyamide networks

The aqueous solution containing PIP (0.5% w/v) and NaOH (0.1% w/v) was adjusted with hydrochloric acid to pH 10. This aqueous solution (100 mL) was poured into a toluene solution of acyl chlorides (0.1% w/v, 100 mL). White solids formed

instantaneously and the mixtures were stirred for 2 min at room temperature. The resultant polymers denoted as TPMC/PIP, TPSC/PIP and TMC/PIP were filtered off, washed with water, methanol and DMF, and dried in vacuo ( $100 \text{ }^\circ\text{C}$ , 10 h) to afford the polyamide networks as a white bulk. Yield  $\sim 90\text{--}92\%$ .

### 2.3. Fabrication of ultrathin microporous membranes

The ultrathin microporous membranes were prepared using interfacial polymerization technology. First, the aqueous solution containing PIP (0.5% w/v), NaOH (0.1% (w/v)) and sodium dodecyl sulfonate (SDS) (0.05% w/v) was adjusted to pH 10 by hydrochloric acid. Then this aqueous solution was poured on the surface of the support membrane and allowed to remain for 2 min after which the excess solution was drained from the soaked surface and the membrane was air-dried at room temperature. Next, an organic solution (toluene) of acyl chloride (0.1% w/v) was applied, the excess solution was drained and the membrane formed instantly. Finally, the membrane was stored in distilled water until it was tested.

### 2.4. Characterization methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on the Bruker Avance 300 or 600 MHz spectrometer. The FT-IR spectra were obtained using a Bruker Vertex 70 spectrometer at a nominal resolution of  $2 \text{ cm}^{-1}$ . The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku Max 2500 V PC X-ray diffractometer with  $\text{Cu K}\alpha$  radiation at a wavelength of  $1.54 \text{ \AA}$  (40 kV, 200 mA) with a scanning rate of  $5^\circ/\text{min}$  from  $10$  to  $50^\circ$ . All solid-state NMR experiments were performed on a Bruker Avance III 400 WB spectrometer equipped with a 9.39 T magnet at 297 K. The  $^1\text{H}\text{--}^{13}\text{C}$  cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded using a Bruker 4 mm standard bore MAS probe head with the  $\text{ZrO}_2$  rotors spinning at 12 kHz rate with a Larmor frequency of 100 62 MHz. A total of 5000 scans were recorded with a 6 s recycle delay for each sample. All  $^{13}\text{C}$  CP/MAS chemical shifts were referenced to the resonances of adamantane standard ( $\delta = 29.5 \text{ ppm}$ ). The  $^{29}\text{Si}$  CP/MAS spectra were recorded using a Bruker 7 mm standard bore MAS probe head with the  $\text{ZrO}_2$  rotors spinning at 5 kHz rate with a Larmor frequency of 79.50 MHz. A total of 1500 scans were recorded with a 3 s recycle delay for each sample. All  $^{29}\text{Si}$  CP MAS chemical shifts were referenced to the resonances of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) standard ( $\delta = 0$ ).  $\text{N}_2$  and  $\text{CO}_2$  adsorption isotherms were measured by Quantachrome Instruments at the designated temperature. A sample of  $\sim 100 \text{ mg}$  was used for the adsorption measurements and was maintained at either 77 K with liquid nitrogen, at 273 K with an ice-water bath or at 298 K with a water bath for  $\text{CO}_2$  and  $\text{N}_2$  adsorption isotherms. The amount of gas adsorbed on each sample was measured for single component pure gas. The ideal adsorption selectivity between  $\text{CO}_2$  and  $\text{N}_2$  was calculated by interpolating the adsorption of the sample at 1 bar and determining the ratio [34]. Before adsorption measurements, all the samples were degassed in vacuum for 10 h at  $100 \text{ }^\circ\text{C}$ . The nanofiltration (NF) performance tests were conducted using a cross flow filtration system with an effective membrane area of  $20.4 \text{ cm}^2$  at 0.4 MPa. The salt rejection rate was measured by the salt concentration in the permeation and the feed using an Elmeiron conductivity meter CC-501 (Poland). The desalination rate was calculated by using the following equation:

$$R_j(\%) = \left(1 - c_p/c_f\right) \times 100$$

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