Journal of CO_2 Utilization 19 (2017) 214–220

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Robust microporous organic copolymers containing triphenylamine for high pressure CO_2 capture application

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ARTICLE INFO

Keywords:
Microporous organic polymers
Pre-combustion CO_2 capture
H_2 purification
Pressure-swing adsorption (PSA)
Ideal adsorbed solution theory (IAST)

ABSTRACT

Various adsorbents including zeolites, activated carbon and metal-organic frameworks have demonstrated a potential capability for applications in pre-combustion carbon capture and H_2 purification owing to their large surface areas and affinity for CO_2. However, most adsorbents showing promising performances in dry condition are not stable or lose their capability for capturing CO_2 in the presence of H_2O and acidic gases such as H_2S. To address this issue, a series of triphenylamine-containing microporous organic copolymers (PP-N-*x*) possessing high surface areas (1010–1251 $m^2 g^{-1}$) as well as excellent hydrolytic and acid stability were synthesized and evaluated for potential application in high pressure CO_2 capture above-mentioned. Among the adsorbents tested, PP-N-25 exhibited the highest CO_2/H_2 selectivity over the entire pressure range along with the good CO_2 uptake capability which is comparable to HKUST-1, a commercial metal-organic framework possessing coordinatively open metal sites. Subsequent breakthrough experiment revealed that PP-N-25 maintains decent CO_2 adsorption capability even in the presence of H_2O while HKUST-1 lost CO_2 capturing capability in humid condition.

1. Introduction

Implementation of carbon capture and sequestration (CCS) technology in the coal-fired power plants, which accounts for ∼67% of reported CO_2 emission, is depicted to be an effective way to reduce CO_2 emission, which is the main cause of global warming and associated environmental issues such as extreme weather conditions, rise in sea level and loss of ecosystem [1–4]. To address this urgent issue, various approaches including oxy-fuel combustion, post-combustion capture, and pre-combustion capture have been proposed as means to reduce CO_2 emission [1,5]. In the case of oxy-fuel combustion, the cost of pure O_2 production has been a limiting factor as air separation is energy intensive owing to the similar properties of O_2 and N_2. Meanwhile, post-combustion capture removes CO_2 from flue gas that contains predominantly CO_2, N_2 and water vapor after the combustion of coal with excess air. In this scenario, factors limiting implementation of the technology were found to be the low partial pressure of CO_2 (c.a. 15 mol% at 1 bar) and the large volume of flue gas that must be treated [6]. Pre-combustion CO_2 capture on the other hand is the strategy for zero CO_2 production during the combustion step by decarbonating fuel gas prior to combustion [5]. In this process, the coal is first broken down into synthesis gas composed of H_2 and CO. Subsequently, the water-gas shift reaction is carried out to produce a mixture containing H_2, CO_2, and H_2O together with other gases such as H_2S in trace concentration [5,7–10]. In comparison to flue gas produced in conventional power plant, the mixture gas produced by water-gas shift reaction is at a very high pressure with larger concentration of CO_2 that provides a sufficient driving force for CO_2 capture. As such, CO_2 capture can be readily conducted via pressure swing adsorption (PSA) with solid adsorbent, which can treat the gas with higher processing rate with less energy consumption than temperature swing adsorption [11,12]. Moreover, such high pressure CO_2/H_2 separation with solid adsorbents can be applied to other industrial processes such as hydrogen purification in steam reforming process [5].

Overall system efficiency and economic feasibility of PSA process for CO_2/H_2 separation are largely dependent on the performance of solid adsorbent employed. Thus, several pertinent criteria have been applied to evaluate solid adsorbents for pre-combustion CO_2 capture: (1) CO_2 working capacity, which is a measure how much CO_2 can be treated in one adsorption-desorption cycle and can be defined as the difference of the adsorption amounts at high and low pressures; (2) CO_2/H_2 selectivity that determines the purity of CO_2 in adsorbed phase; and (3) stability under real operating conditions, especially towards H_2O and acidic gases such as H_2S [13]. Conventional solid adsorbents

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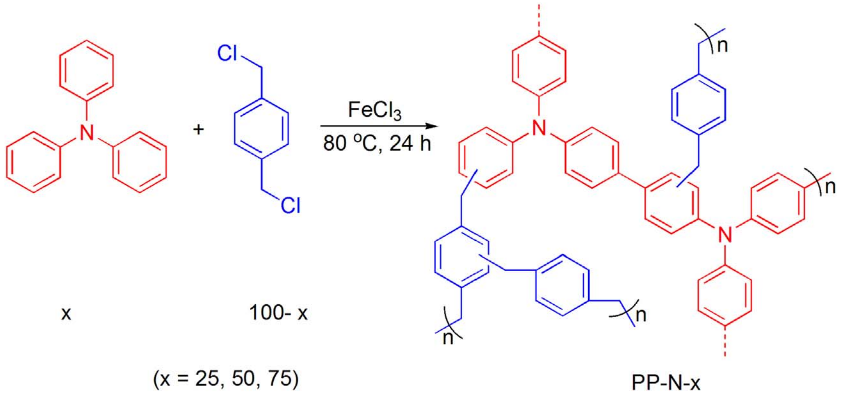
http://dx.doi.org/10.1016/j.jcou.2017.03.020
Received 17 January 2017; Received in revised form 7 March 2017; Accepted 31 March 2017



Scheme 1. Synthesis of PP-N-*x*.

including zeolites and activated carbons often fail to meet these requirements due to their low working capacities and/or poor CO_2/H_2 selectivity [5,7,14].

Recently, Long and coworkers evaluated a series of well-known metal-organic frameworks (MOFs) as adsorbents for pre-combustion CO_2 capture and H_2 purification [15]. The result showed that MOFs with coordinatively open metal sites are the most promising candidates for CO_2/H_2 separation due to their high selectivity and large working capacity [15]. However, in their study, the working capacity was overestimated by assuming the gas phase composition in the column at 1 bar of desorption pressure is same as feed gas composition, which resulted in much lower CO_2 partial pressure than the true pressure in real condition. Note that, in desorption condition, the whole adsorbent column is nearly saturated with high purity CO_2 which is released from the adsorbents. Besides, the effect of H_2O on the CO_2 capture capability as well as the structural stability of the adsorbents was not investigated. It is noteworthy that water vapor which possesses a strong dipole moment has a much greater affinity for the open metal sites than CO_2 does [16]. Furthermore, a vast majority of MOFs suffer from long-term hydrolytic instability due to the insufficient strength of coordination bonding between metal center and ligand. This limits the potential practicability of MOFs in industrial gas separation processes as the complete removal of moisture prior to PSA operation is not economically feasible in many cases.

Meanwhile, microporous organic polymers (MOPs) such as polymers of intrinsic microporosity (PIMs) [17], hypercrosslinked polymers (HCPs) [18], conjugated microporous polymers (CMPs) [19], and covalent organic frameworks (COFs) [20] are the emerging class of adsorbents featuring high porosity and diverse functionality. This class of materials can possess better chemical stability than MOF when the framework is constructed by strong covalent bonding. However, most of studies on MOPs thus far have been focused on CO_2 uptake at low pressure range considering post-combustion carbon capture as a potential application [21–27]. Despite a couple of studies on high pressure CO_2 uptake properties of MOPs were reported, important parameters for industrial PSA operation such as working capacity have not yet been evaluated [18,28,29].

In this study, a series of triphenylamine-containing MOPs (denoted as PP-N-*x*) that are known to have a decent affinity for CO_2 was synthesized [30], and evaluated for potential application in pre-combustion CO_2 capture and H_2 purification. These materials are expected to be ideally suited for these applications due to their high surface areas, good affinity for CO_2, excellent thermal and chemical stability, as well as low production cost [30,31]. The potential utility of PP-N-*x* for high-pressure CO_2/H_2 separation was thoroughly investigated via both equilibrium gas uptake analysis and dynamic breakthrough experiment in humid condition. The performances of our copolymers were also compared with other conventional adsorbents such as HKUST-1, ZIF-8 and an activated carbon. HKUST-1 and ZIF-8, which are currently commercially available, represented MOF adsorbents with and without coordinatively open metals sites, respectively.

2. Experimental

2.1. Materials

Triphenylamine (TPA), dichloro-*p*-xylene (DCX), anhydrous $FeCl_3$, and activated carbon (AC; Darco®) were purchased from Sigma Aldrich. 1,2-Dichloroethane (DCE) was dried over CaH_2 prior to use. Other chemicals were used as received without further purifications. Two model MOF adsorbents, HKUST-1 and ZIF-8, were synthesized based on the procedure reported elsewhere [32,33].

2.2. Synthesis of triphenylamine-containing porous copolymers

A series of PP-N-*x* (*x* represents the molar percent of triphenylamine) was synthesized with TPA and DCX as shown in Scheme 1 [18,30]. For the synthesis of PP-N-25, anhydrous $FeCl_3$ (13.2 mmol, 2.141 g) was added to a solution made up of TPA (2.0 mmol, 0.491 g), DCX (6.0 mmol, 1.050 g) and DCE (60 mL) under nitrogen atmosphere. Subsequently, the mixture was stirred at 80 °C for 24 h. After the reaction, the solid obtained was filtered and thoroughly washed with methanol and tetrahydrofuran until a clear filtrate was observed. The resulting PP-N-25 was then dried in vacuum oven at 100 °C for 24 h (yield = 79.3%). Using the same procedure, other porous copolymers were also synthesized from the solutions with different TPA to DCX ratios.

2.3. Characterization

The FT-IR spectra were obtained using a PerkinElmer Spectrum One spectrometer at a nominal resolution of 2 cm^{-1} in the range of 4000 to 500 cm^{-1}. Nitrogen physisorption at 77 K was performed on an Autosorb–6 B instrument (Quantachrome). Single component CO_2 and H_2 adsorption isotherms were measured by a high-pressure gas sorption analyzer (Quantachrome, iSorb HP1). In a typical measurement, c.a. 0.2 g of sample was loaded into the adsorption cell. After activation of the PP-N-*x* at 120 °C for 15 h under high vacuum, pure component CO_2 and H_2 isotherms were obtained in a pressure range of 0–20 bar (0–40 bar for H_2) at 40 °C which is precisely controlled by an isothermal jacket. Other conventional adsorbents, namely HKUST-1, ZIF-8 and an AC, were activated at 180 °C for 15 h under high vacuum before sorption testing.

2.4. Evaluation of adsorbents in pre-combustion CO_2 capture and H_2 purification process

Gas adsorption isotherms obtained were first fitted with the