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Effect of Diaminopropane on Formation of Triazine-based Covalent Organic Polymer for CO_2 Capture

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Abstract

Polyamine triazine based Covalent Organic Polymer (COP) was synthesized using catalyst free polycondensation method, called Covalent Diamino Polymer (CDAP). 1,3-diaminopropane was selected as the organic linker and the CO_2 adsorption capacity was studied. CDAP was characterized with Fourier Transform Infra-red spectroscopy (FTIR) and N_2 adsorption desorption measurement. A comparison of the characteristics and CO_2 adsorption capacity was made between COP-1 and CDAP. This study found that the structure of organic linkers greatly influences the properties of organic polymer as well as the CO_2 uptake capability.

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Keywords: COP; diamine; triazine; polymer; CO_2

1. Introduction

CO_2 has been regarded as the primary anthropogenic greenhouse gas. A sharp growth of anthropogenic CO_2 concentration raises a concern on global climate change issue in the past two decades [1] . Therefore, emerging of an efficient and economical CO_2 capture and separation technology is an imperative task to reduce anthropogenic CO_2 emission. However, amine-based absorption which is the conventional absorption for CO_2 removal process is energy intensive and costly. Furthermore, the bulk utilization of toxic and harmful chemical solvent is environmentally-destructive [2].

Several alternative separation technologies such as adsorption, membrane and cryogenic separation have been studied in order to overcome the flaws. Adsorption have been considered as a practical technology approach for CO_2 removal because of the low energy requirement, profitable process and ease of applicability over a relatively wide range of temperature and pressure [3, 4].

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A variety of solid adsorbents such as zeolites, activated carbon, mesoporous silica and metal organic frameworks (MOFs) have been widely studied for CO_2 capture [2, 5, 6]. However, the reported adsorbents which inherit several drawbacks like low selectivity in operation and highly sensitive to moisture present have been limited their practicability for CO_2 separation.

Covalent organic materials (COMs) [7-10] are being generated at a rapid and growing pace due to its high porosity, diversified synthetic conditions as well as good physicochemical stability. Among of them, the specific chemical functionality in covalent organic polymer (COP) showed promising CO_2 adsorption capacity. The major advantage of COPs over than others is the low sensitivity to moisture and high thermal stability because of the relatively stable covalent C-C, C-H and C-N bonds [11, 12].

CO_2 uptake of these porous polymers can be enhanced by tuning the pore size, BET surface area and incorporating nitrogen rich functionality in the framework [13-15]. In 2012, Patel et. al. [12] have developed a method to synthesis COP using one-pot polycondensation under catalyst free condition. Interestingly, it was reported that the moderate BET specific surface area of COP-1 exhibited promising CO_2 uptake i.e 1.38 mmol/g at 298 K/1 bar. Furthermore, it was inherited high recyclability and excellent hydrothermal stability.

COP-1 was synthesized by coupling of nitrogen rich triazine units and piperazine, a cyclic type diamine. Triazines with high nitrogen content is a desirable feature for CO_2-specific gas operations [16]. Chloride centers of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) is highly reactive and easily replaced with amines to give triazine-based COP via nucleophilic substitution. Because of the various possibilities of substitution on the triazine ring, the properties of the resulting polymers are widely influenced by the geometry structure of organic linkers [17, 18].

Braun et. al. [18] reported a series of polyamines with triazine-based polymers using interfacial polycondensation reaction. It was found that amine linkage, N-H was formed on the chemical structure when primary amines were chosen. The interesting polymer structure may offer the opportunity to enhance CO_2 uptake by facilitating the acid-base interactions between N-containing basic functional group and acidic CO_2 molecules.

Therefore, this study is to perform an investigation of a polyamines with triazine based COP on CO_2 uptake. Polyamines with triazine based COP is synthesized through catalyst free polycondensation as Patel et. al. [12] reported where 1,3-diaminopropane is selected as the organic linker in this study.

2. Methodology

Cyanuric chloride (CC), piperazine (anhydrous), N,N-diisopropylethylamine (DIPEA) and 1,3-diaminopropane ($\geq$ 99%) were purchased from Sigma Aldrich, USA. Dry 1,4-dioxane solvent with $\leqslant$0.005% water content and ethanol were purchased from Merck Milipore.

2.1. Synthesis of COP-1

CC (2.50 g, 13.6 mmol) was dissolved in dry 1,4 dioxane (40 mL). The solution was then added dropwise to a solution of piperazine (1.87 g, 21.7 mmol) and DIPEA (9.0 mL) in 1,4-dioxane (60 mL) with continuous stirring at 288 K under Ar atmosphere. The resulting white mixture was stirred at 288 K for 1 h and then for a further with 2 h at 298 K and then 21 h at 358 K. The off-white precipitate formed was washed with 1,4-dioxane and soaked with ethanol three times over a period of 12 h. COP-1 was obtained after the off-white slurry was dried at room temperature under vacuum for 2 h.

2.2. Synthesis of CDAP

CC (2.50 g, 13.6 mmol) was dissolved in dry 1,4 dioxane (40 mL). The solution was then added dropwise to a solution of 1,3-diaminopropane (0.75 g, 10.2 mmol) and DIPEA (9.0 mL) in 1,4-dioxane (60 mL) with continuous stirring at 288 K under Ar atmosphere. The resulting white mixture was stirred at 288 K for 1 h and then for a further with 2 h at 298 K and then 21 h at 358 K. White precipitate formed was washed with 1,4-dioxane and soaked with ethanol three times over a period of 12 h. COP-1 was obtained after the white slurry was dried at room temperature under vacuum for 2 h.

2.3. Material Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by Thermo Scientific Nicolet iS 10 FT-IR Spectrometer for COP-1 and CDAP using ATR technique. N_2 adsorption desorption measurement and CO_2 adsorption were performed using Mini Belsorp II at 77 K and 298 K respectively, after the samples had been degassed at 428 K for 5 h.

2.4. CO_2 Adsorption Measurement

CO_2 measurement for COP-1 and CDAP was performed using mini BELSORP-Mini II at 298 K in a water bath. Both of the samples were dried at 428 K under vacuum for 5 h prior to adsorption measurement.