

Functionalisation of Poly(High Internal Phase Emulsion) with Amine for CO₂ Capture

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An excellent porous material was prepared from vinylbenzyl chloride (VBC) and divinylbenzene (DVB) via high internal phase emulsion (HIPE) technique and introduced with heterocyclic amines (piperazine or PZ, hydroxyethylpiperazine or HEP and aminoethylpiperazine or AEP) by post-functionalization for using as adsorbents in CO₂ capture applications. The reaction between the amine functional group and adsorbent was confirmed by Fourier transform infrared spectroscopy. The disappearance of C-Cl bonding at 1,265 cm⁻¹ and 710 cm⁻¹ and the presence of N-H bonds at 3,400 cm⁻¹ and 1,670 cm⁻¹ were observed. The influence of the amine structure on the surface area and the conversion reaction of polyHIPE were investigated by surface area analysis and elemental analysis. In the CO₂ adsorption step, the feed gas concentration was 4 vol% of CO₂/N₂ with a flow rate of 5 mL/min, and was carried out at 298 K. The CO₂ concentration was continuously determined by gas chromatography. The dynamic adsorption capacity of PZ-HIPE, HEP-HIPE, and AEP-HIPE were 0.112, 0.057, and 0.074 mmol CO₂/mmol amine compound.

1. Introduction

Emission of CO₂, which is one of the major greenhouse gases (GHG), contributes to global warming. Various techniques have been developed to minimize the emission of GHG, such as cryogenic capture, membrane technology, absorption technology, adsorption technology, as well as a microbial/ algal process system (Gupta et al., 2003) and later (Peter and Abdelhamid, 2007). A typical technology widely used to separate CO₂ in gas processes is absorption using aqueous alkanolamines based on reversible reaction of CO₂ via an acid-base reaction. Unfortunately, the alkanolamine solution presents some problems, i.e. oxidation degradation, high corrosion, foaming in the gas-liquid interface, and large amounts of energy are required for regeneration. Adsorption, an alternative method, has been proposed to capture CO₂. There are various kinds of adsorbents used, activated carbon (Zhijuan et al., 2010), zeolite 13X-Ca (Chou et al., 2013), SBA-15 mesoporous silica (Chang et al., 2009), and MCM-41 mesoporous molecular sieve (Hsu et al., 2010). In addition, the capacity of the adsorbents can be improved by introducing amine functional groups into the adsorbents via grafting or impregnating with diverse amine species. However, the using of these conventional adsorbents still has some problems. They do not actually gain a benefit from large contact area for CO₂ adsorption due to pore plugging after amine modification, which reduces surface area and becomes restricted to diffusion. Fortunately, a material prepared by high internal phase emulsion contains very high surface area, high porosity and well-connected pores which provide high contact area and rapid CO₂ permeability throughout the material (He et al., 2012). Furthermore, amines could potentially be introduced during emulsion polymerization via chemical reaction and become a part of the structure (Dejburum et al., 2012); thus, eliminate the pore plugging as occurs with grafting or impregnation. These reasons brought about to the interest of polyHIPE in CO₂ adsorption application. In this research, polyHIPE was prepared in water in oil emulsion system using divinylbenzene (DVB) and vinylbenzyl chloride (VBC) providing reactive handle group available for collaborating with amines in order to enhance the capacity of the adsorbent and study the effect of amine types on the CO₂ adsorption.

2. Experimental

2.1 Preparation of amine-modified porous polymer by high internal phase emulsion technique

Together 0.35 mL of vinylbenzyl chloride (VBC, Aldrich), 0.65 mL of divinylbenzene (DVB, Merck) 1 mL of chloroethylbenzene (CEB, Aldrich) 0.36 g of sorbitanmonooleate (Span80, Aldrich), 0.0229 g of dodecylbenzene sulfonic acid sodium salt (DDBSS, Aldrich) and 0.0171 g of cetyltrimethylammonium bromide (CTAB, Fluka) were mixed together as an oil phase. An aqueous solution was separately prepared by mixing 18 mL of distilled water, 0.04 g of $K_2S_2O_8$, and 0.2 g of $CaCl_2 \cdot 2H_2O$. It was slowly added to the oil phase under constant agitation. The emulsion was stirred at room temperature for 1 h, poured into a cylindrical plastic mold (2 cm diameter) and put into a water bath for polymerization at 70 °C for 24 h. The material was removed from the mold and extracted with hot ethanol (EtOH) in a soxhlet extractor for 6 h and dried to a constant weight in an oven at 60 °C for 48 h. The monolithic material was cut into a 2 cm length and used for functionalization with the amine. A piece of the material (0.4 g, 0.876 mmol) was immersed in the amine solution which was prepared by mixing 2.629 mmol of amine (0.227 g of piperazine (PZ, Merck), 0.323 mL of hydroxyethylpiperazine (HEP, Merck), and 0.343 mL of aminoethylpiperazine (AEP, Merck)) in 10 mL of dimethylformamide (DMF). The resulting mixture was left at room temperature for 1 h and then put in a water bath at 80 °C for 24 h. After the reaction completed, the sample was filtered and washed with DMF, EtOH, EtOH/ H₂O (1:1 v/v), EtOH/ tetrahydrofuran (THF) (1:1 v/v), and THF, respectively, left at room temperature for 1 h and dried in a vacuum oven at 60 °C for 24 h.

2.2 Characterization

The morphology of material was investigated by field emission scanning electron microscopy (FE-SEM) and the specimens were coated with thin layer of platinum under vacuum before analysis. The specific surface area was determined by N₂ adsorption/desorption isotherm on a Quantachrome Autosorb 1-MP, where the sample was degassed at 110 °C prior to analysis. All amine-modified materials were investigated for the functionalization reaction by Fourier transform infrared spectroscopy (FTIR) using KBr pellets. The degree of conversion of amine functionalization was determined by CHN elemental analysis and chloride titration. For chloride titration, polyHIPE powder was mixed with 5.5 mL of pyridine and stirred at 100 °C for 2 h. After cooling, 10 mL of DMF and 7 mL of 65 % nitric acid were added and the volume was adjusted to 100 mL with distilled water. The sample solution (20 mL) was added with 1 mL of 0.1 M silver nitrate (AgNO₃) and 1 mL of Fe³⁺ and an excess AgNO₃ was titrated with 0.01 M of potassium thiocyanate (KSCN). The amount of chloride in the sample was calculated from the volume of KSCN used and AgNO₃ added.

2.3 CO₂ adsorption study

The schematic diagram of the experimental setup for CO₂ adsorption study is shown in Figure 1. Before doing the adsorption experiment, the adsorbent in the reactor was pretreated with a N₂ flow (20 mL/min) at 60 °C and then cooled down to room temperature, and the N₂ flow was then switched to 4 vol% of CO₂ in N₂ balance with a total flow rate of 5 mL/min. The concentration of CO₂ was continuously detected by gas chromatography (GC) until the adsorption breakthrough point reached equilibrium. The dynamic adsorption capacity of the adsorbent can be calculated from Eq(1).

$$Q_{ads} = \frac{FC_{in}t_{st}}{M} \quad (1)$$

where Q_{ads} is the dynamic adsorption capacity, mmolCO₂/g; F is total flow rate, mol/min; C_{in} is the concentration of CO₂ entering the reactor, vol%; M is the weight of the adsorbent, g; and t_{st} is the stoichiometric time corresponding to CO₂ stoichiometric adsorption capacity, min, which can be estimated from the breakthrough profile according to Eq(2).

$$t_{st} = \int_0^t \left(1 - \frac{C_{ou}}{C_{in}}\right) dt \quad (2)$$

Where C_{ou} is the CO₂ concentration downstream of the reactor, vol%; t is the time at which the C_{ou} reached its maximum permissible level, min.

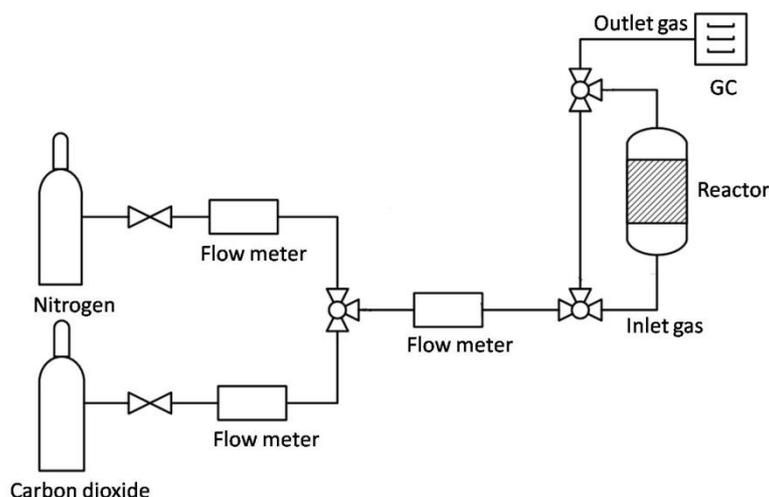


Figure 1: CO₂ Experiment set-up for dynamic CO₂ adsorption measurement

3. Results and Discussion

3.1 Preparation of amine-modified porous polymer by high internal phase emulsion technique

A porous polymer template for amine modification was easily prepared via high internal phase emulsion by dispersing the aqueous phase into the stirring oil phase to get an emulsion. After polymerization took place and the internal phase (water) was removed from the polymer matrix, thus, a porous polymer was obtained. This monolithic material, prepared from VBC and DVB (poly(VBC/DVB)HIPE or polyHIPE), showed a unique open cellular structure with high porosity and a high degree of connectivity (Figure 2). This polyHIPE had 152 m²/g surface area, 0.31 cm³/g pore volume, and 169 nm pore size. The reactive handle group (methylene chloride, CH₂-Cl) of VBC was functionalized with an amine compounds through a nucleophilic substitution reaction that could take place at two different nucleophilic groups, i.e. at hydroxyl and amine for HEP and two amine for AEP. Finally, the nucleophilic substitution reaction of VBC with HEP or AEP yielded the product mixture as shown in Figure 3. The reaction between the methylene chloride group of VBC and the amine group (or hydroxyl group) of amines was confirmed by observing the disappearances of C-Cl wagging (1,265 cm⁻¹) and stretching (710 cm⁻¹) vibrations and the presence of N-H stretching (3,400 cm⁻¹) and bending (1,670 cm⁻¹) vibrations, as shown in Figure 4. FTIR spectra confirmed the modification of all amines in the polyHIPE.

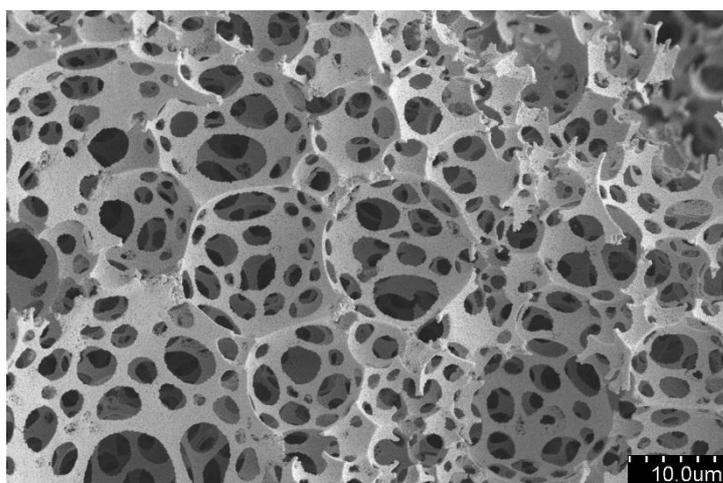


Figure 2: Surface morphology of poly(VBC/DVB)HIPE (×3000)

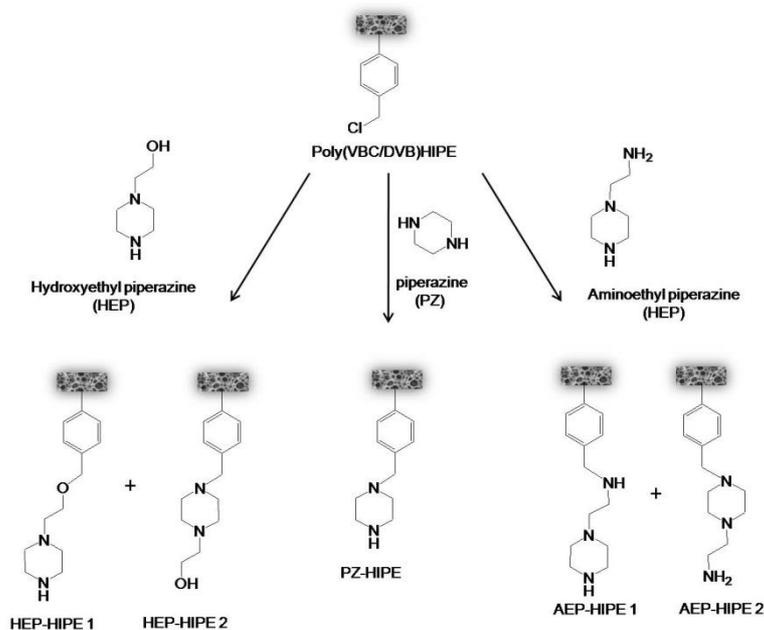


Figure 3: Nucleophilic substitution reactions of all amines on polyHIPE

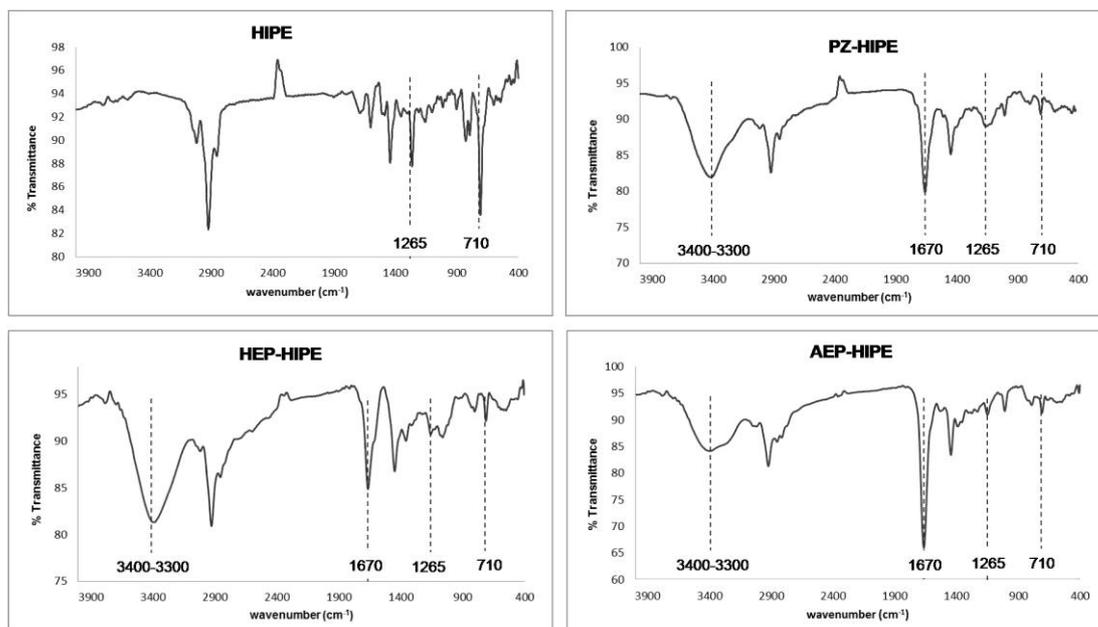


Figure 4: FTIR spectra of amine functionalized polyHIPEs

To assure the accuracy of the conversion degree of amine functionalization in the adsorbent (see Table 1), the unreacted chloride of VBC was determined by titration (Eq(3) and % conversion A) and the addition of amine nitrogen by CHN analysis (Eq(4) and % conversion B). The average conversion of PZ-HIPE of 91.01 % means that 91.01 % VBC completed the nucleophilic substitution reaction with the amine of PZ. The order of the substitution was PZ-HIPE > HEP-HIPE > AEP-HIPE. The difference in the degree of conversion was due to different amine compounds exhibiting different penetration abilities into the polyHIPE to react with the reactive chloride group. The steric hindrances of HEP and AEP (molecular models are shown in Figure 5) are more hindered than that of PZ; thus, PZ had to be the highest degree of conversion (91.01 %). The amine modification also affected the surface properties of the adsorbent (Table 2). There was a reduction of surface area, pore volume and pore size due to the partial blockage of the

amine compound on the pores at the external and internal surface of the material. This phenomenon also confirms the modification of amine in the material. The surface area of the modified material was dependent on the loading of amine compound. Due to the small amount of amine compound loading of AEP (1.57 mmol/g, see Table 2) in the polyHIPE, there was the smallest reduction of surface area (97 m²/g) when compared to the others (32 m²/g of PZ-HIPE and 60 m²/g of HEP-HIPE).

$$\% \text{Conversion A} = \frac{\text{Chloride}_{\text{origin}} - \text{Chloride}_{\text{remaining}}}{\text{Chloride}_{\text{origin}}} \times 100 \quad (3)$$

$$\% \text{Conversion B} = \frac{\text{Nitrogen}_{\text{found}}}{\text{Nitrogen}_{\text{calculated}}} \times 100 \quad (4)$$

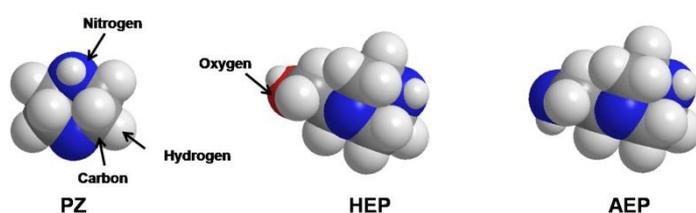


Figure 5: Molecular models of piperazine and its derivative

Table 1: Elemental analysis data and degree of conversion of amine functionalization

Adsorbent	Chloride (A) (mmol/g)	Nitrogen (B)(mmol/g)		% Conversion		
		Found	Theoretical	A	B	Average
PolyHIPE	2.25	-	-	-	-	-
PZ-HIPE	0.19	4.08	4.504.106.16	91.48	90.55	91.01
HEP-HIPE	0.44	3.25		80.37	79.31	79.84
AEP-HIPE	0.11	4.71		78.89	76.43	77.66

Table 2: Surface properties, amine loading and adsorption capacity of amine-modified materials

Material	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Amine compound loading (mmol/g)	Adsorption capacity	
					(mmol CO ₂ /g)	(molCO ₂ /mol amine compound)
HIPE	152	0.31	169	-	0.106	-
PZ-HIPE	32	0.07	104	2.04	0.151	0.074
HEP-HIPE	60	0.15	130	1.63	0.092	0.056
AEP-HIPE	97	0.20	150	1.57	0.228	0.112

3.2 CO₂ adsorption study

The CO₂ adsorption experiments were performed at room temperature and the data of the CO₂ concentration was collected continuously by GC and plotted as a breakthrough profile to calculate the dynamic adsorption capacity (Q_{ads}). PZ, HEP, and AEP were used to incorporate with the polyHIPE in order to enhance the adsorption capacity. The adsorption capacity of HEP-HIPE (0.092 mmol CO₂/g) material was lower than that of bare polyHIPE (0.106 mmol CO₂/g) due to the mixture of HEP-HIPE1 and HEP-HIPE2 (Figure 3). HEP-HIPE2 could not directly adsorb CO₂ as its structure contained tertiary amine, which could not directly react with CO₂ to produce carbamates mechanism in a dry condition, while HEP-HIPE1 contains secondary amine, which follows the carbamate mechanism. In addition, the surface area

of HEP-HIPE (60 m²/g) was much less than that of the bare polyHIPE (151 m²/g); however, HEP-HIPE had a slightly lower adsorption capacity. The carbamate mechanism explains the reaction between CO₂ and amine via the formation of carbamate species, i.e. zwitterions intermediate, following by the removal of a proton (Zelenak et al., 2008). Primary and secondary amines carry free protons on the nitrogen atom, which can yield the mechanism while tertiary amine can't. Thus, AEP-HIPE containing both primary and secondary amines in the structure resulted in the highest CO₂ adsorption capacity (0.112 mol CO₂/ mol amine compound), while PZ-HIPE containing only secondary amine showed lower adsorption capacity (0.074 mol CO₂/ mol amine compound). HEP-HIPE showed the adsorption capacity of 0.056 mol CO₂/ mol amine compound because it contained one secondary amine. The performance of heterocyclic amine for CO₂ adsorption was in the order of AEP > PZ > HEP.

4. Conclusions

Heterocyclic amines (piperazine and its derivatives) were post-functionalized onto a porous polymer material in order to enhance CO₂ adsorption capacity. Only PZ and AEP (except HEP) could enhance the adsorption capacity compared to the bare polyHIPE material. The adsorption capacity of the material depended on the type of amine group which decreased in the order of primary > secondary > tertiary amine containing in the adsorbent so the order of the efficiency of the amine-modified adsorbent is AEP-HIPE > PZ-HIPE > HEP-HIPE.

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