

Adsorption of carbon dioxide on ionic liquids-modified active carbons and amino-modified polymer

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(Received 7 April 2010 • accepted 3 June 2010)

Abstract—Active carbons with various particle sizes (38-150, 300-500 and 800-1,200 μm) were modified by ionic liquids (ILs), and organic polymer was modified by acrylamide using a simple procedure, and these materials were applied to capture carbon dioxide (CO_2). The CO_2 adsorption amounts were calculated using a mass balance equation at three different temperatures (298.15, 308.15 and 318.15 K), respectively, and the influences of gas pressure, particle size and temperature on adsorption were discussed. Experimental results showed that the CO_2 adsorption capacity of ILs-modified active carbons was better than amino-modified polymer, and the smaller particle size (38-150 μm) ILs-modified active carbons had the largest adsorption capacity at 298.15 K. Compared with previous research about polyethyleneimine (PEI)-modified silica gel, the adsorption amount of CO_2 on ILs-modified active carbons has been greatly improved with lower cost.

Key words: Adsorption, Carbon Dioxide, Ionic Liquids, Active Carbons, Polymer

INTRODUCTION

Carbon dioxide (CO_2) is a key global warming gas that is proposed to have direct linkage to global climate changes [1,2]. Therefore, there is a growing interest in developing technologies for efficient capture and sequestration of large quantities of CO_2 . An efficient and economical capture material is needed to capture and separate the CO_2 produced during various industrial processes.

Ionic liquids (ILs), organic salts with a low melting point (<373.15 K), have been emerging as nonvolatile and reversible CO_2 absorbents for CO_2 capture [3-6]. Bates et al. developed a task-specific ionic liquid for CO_2 capture by introducing an amine group to the ionic liquid, substantially increasing its CO_2 solubility [4]. In general, active carbons are widely used as selective adsorbents for gas separation, and they have some advantages of shape selectivity for planar molecules, high hydrophobicity, and stability at higher temperatures [7,8]. Because CO_2 is an acidic gas, a basic group such as amino group can lead to preferential adsorption of CO_2 . Amino-modified polymer with low cost is desired to be one of the key CO_2 capture materials [9,10].

To continue previous studies about CO_2 absorbent [11] and further reduce cost, active carbons with various particle sizes (38-150, 300-500 and 800-1,200 μm) were modified by ILs and organic polymer was modified by acrylamide using a simple procedure with lower cost than polyethyleneimine (PEI)-modified silica gel for capture of CO_2 in this study.

EXPERIMENTAL

1. Reagents and Materials

Active carbons with three particle sizes (38-150, 300-500 and 800-1,200 μm) were purchased from Sigma (St Louis, MO, U.S.A.),

and their average specific surface areas were 1,150, 860 and 520 m^2/g , respectively. Methacrylic acid (MAA) and glycidyl methacrylate (GMA) were bought from Sigma (St Louis, MO, U.S.A.). Ethylene glycol dimethacrylate (EGDMA) was purchased from Fluka (Buchs, Switzerland). Dodecanol was purchased from Acros organics (New Jersey, USA). Cyclohexanol and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Junsei Chemical Co. Ltd. (Japan) and refined before use. Acrylamide, methanol was bought from Dusan Pure Chemical Co., Ltd (Ansan, Korea). Chlorobutane was bought from Tokyo Chemical Co. Ltd. (Japan) and imidazole was obtained from Aldrich (Milwaukee, WI, USA). Distilled water was filtered with a vacuum pump and a filter (HA-045; Millipore, Waters, USA) before use. All the other solvents used in the experiment were analytical grade.

2. Preparation of ILs and ILs-modified Active Carbons [12-14]

In a typical reaction, chlorobutane (5 g, 0.054 mol) and imidazole (3.68 g, 0.054 mol) were added to a clean, dry, round bottom flask containing a magnetic stir bar, and then toluene (50 mL) was added as a solvent. The reaction was carried out at 373.15 K for about 12 h. The viscous ILs product was washed several times with cold hexane. The ILs impregnation procedure included the addition of about 5 g of active carbons in a glass beaker containing 50 mL of ILs aqueous solution. The mixture was stirred for 4 h at 373.15 K. The treated active carbons were then filtered, and were washed by water to remove any excess of ILs. The ILs-modified active carbons materials with various particle sizes (38-150, 300-500 and 800-1,200 μm) were obtained and were dried overnight under a nitrogen gas flow at 323.15 K.

3. Preparation of Amino-modified Polymer

First, a mixture consisting of 0.5 mL MAA, 2.0 mL GMA, 3.0 mL EGDMA, 3.0 mL dodecanol, 3.0 mL cyclohexanol, 0.4 g acrylamide and 0.12 g AIBN was placed and stirred in a flask, and it was purged with nitrogen gas for 15 min. After the polymerization

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proceeded at 333.15 K for 24 h, the polymer material was ground and washed by methanol to remove the matrices and other soluble compounds. The amino-modified polymer materials were obtained and were dried overnight under a nitrogen gas flow at 323.15 K. The blank polymer without acrylamide was prepared and treated in an identical manner.

4. CO₂ Adsorption Measurement

The adsorbent was regenerated to eliminate trace impurities under vacuum for at least 12 h using a vacuum pump, and then CO₂ was introduced into the loading cell and adsorption cell. The adsorption amount was calculated using a mass balance equation, and the adsorption equilibrium data were obtained using a static volumetric method. The detailed information about CO₂ adsorption measurement was shown in previous work [11].

RESULTS AND DISCUSSION

The adsorption isotherms of CO₂ on various particle sizes active carbons and ILs-modified active carbons at 298.15 K are plotted in Fig. 1. In general, the adsorption amount of CO₂ decreased with an increase in the particle sizes of adsorbents, and the adsorption amount increased with gas pressure increased, when the gas pressures were between 0.241 and 5.078 atm. The smaller particle size (38-150 μm) ILs-modified active carbons had the largest adsorption capacity (4.256 mmol/g) at 298.15 K, when the gas pressure was 4.663 atm. This was due to the higher surface area of the smaller particle size adsorbent.

Comparing weights of ILs-modified active carbons with original active carbons, the contents of ILs in ILs-modified active carbons were estimated, and were around 105, 70 and 40 mg/g for three particle sizes active carbons, respectively. It indicated that there were some interactions between ILs and active carbons [15]. Fig. 1 also shows that the CO₂ adsorption capacity of ILs-modified active carbons was better than non-modified active carbons. This phenomenon was due to the interactions of the functional groups with CO₂ on the ILs-modified active carbons, and the cation of imidazole in ILs had a positive effect on the CO₂ adsorption [16]. However, the

adsorption amounts of CO₂ on ILs-modified active carbons did not increase significantly with the particle sizes of 38-150 μm and 300-500 μm which have the small pore sizes. It was because the smaller pores of 38-150 μm and 300-500 μm active carbons hard to be impregnated with the viscous ILs in comparison with the 800-1,200 μm active carbons.

Fig. 1 shows a general trend of adsorption amounts of CO₂ on adsorbents increasing with increasing CO₂ gas pressure, due to the increased concentration of CO₂ in the adsorption cell with increased gas pressure, during which the CO₂ contacted not only contact the surface of the adsorbent but also the internal pores. The effect of various temperatures (298.15, 308.15 and 318.15 K) was also investigated, and adsorption curves of CO₂ on 38-150 μm ILs-modified active carbons were shown in Fig. 2. The adsorption amount decreased with increasing the temperature, and the CO₂ adsorption at 298.15 K was better than the others. This can be explained by desorption of CO₂ at relatively high temperatures, and the physical adsorptions usually have a lower adsorption amount at relative higher

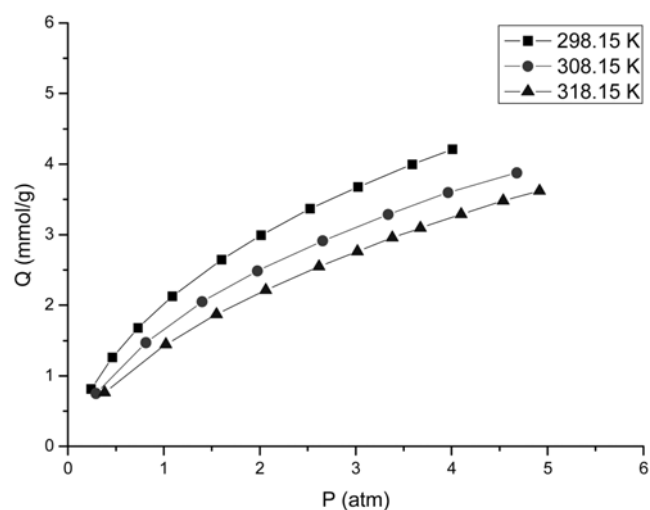


Fig. 2. Adsorption curves of CO₂ on 38-150 μm ILs-modified active carbons at three different temperatures.

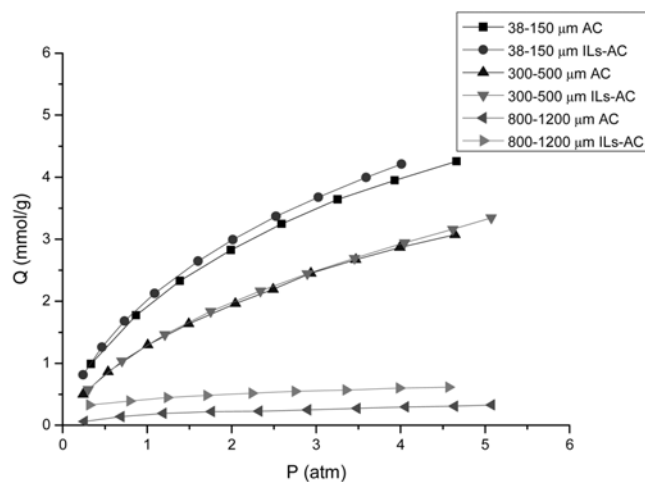


Fig. 1. Adsorption curves of CO₂ on active carbons and ILs-modified active carbons (38-150, 300-500 and 800-1,200 μm) at 298.15 K.

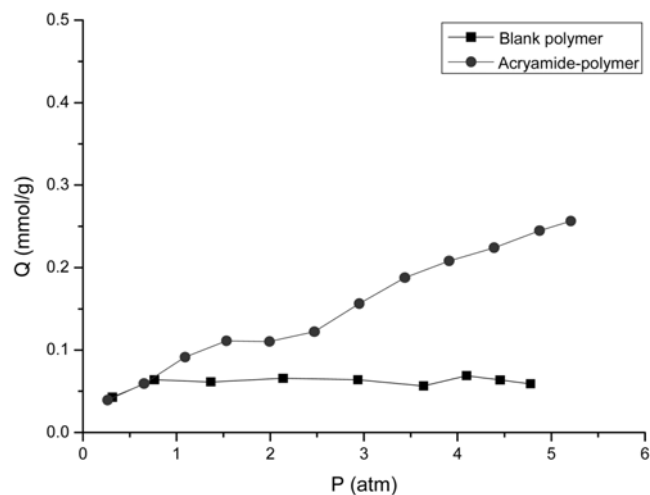


Fig. 3. Adsorption curves of CO₂ on blank and amino-modified polymer at 298.15 K.

temperature.

Besides the imidazolium group in ILs, the amino group was typically used as a functional group for CO₂ adsorption. Fig. 3 shows the adsorption curves of CO₂ adsorption on the blank and amino-modified polymer at 298.15 K. Comparing the blank and ionic liquid polymer, it was found that the CO₂ adsorption capacity of amino-modified polymer was higher than that of blank polymer, and the adsorption amounts increased with the pressure increasing. These phenomena were due to the interactions of the amino functional groups with CO₂, and the gas can penetrate the polymers with the pressure increasing.

CONCLUSIONS

ILs-modified active carbons with various particle sizes (38-150, 300-500 and 800-1,200 μm) and amino-modified polymer were synthesized for capture CO₂. The influences of particle size, gas pressure and temperature on these materials were investigated. The results showed that the CO₂ adsorption capacity of modified active carbons was better than non-modified active carbons, and the adsorption capacity gradually decreased with increasing particle size. The smaller particle size (38-150 μm) ILs-modified active carbons had the largest adsorption capacity at 298.15 K. The CO₂ adsorption amounts of amino-modified polymer were also higher than blank polymer, and the adsorption amounts increased with the pressure increasing. Due to the higher adsorption amounts and lower cost, the ILs-modified active carbons as a potential material for CO₂ adsorption were better than the amino-modified polymer and PEI-modified silica gel [11].

ACKNOWLEDGEMENT

This research was supported by Basic Science Research Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education, Science and Technology (2010-

0015731).

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