



Adsorption and diffusivity of CO₂ in phosphonium ionic liquid modified silica



Jiamei Zhu^{a,b,*}, Feng Xin^a, Junhua Huang^{b,*}, Xiaochen Dong^a, Hanming Liu^b

^a School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou, Jiangsu 221116, PR China

^b Energy Technology, CSIRO, BOX 312, Clayton South, VIC 3169, Australia

HIGHLIGHTS

- For IL modified silica, CO₂ adsorption depends on the porous nature of the silica.
- The IL phases act as a selecting film which notably improves CO₂/N₂ selectivity.
- The grafting method provides a good IL retention with gas cycling.
- Diffusion coefficient in modified silica is in range of 10⁻⁸–10⁻⁷ m²/s using HSDM.

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ABSTRACT

This work investigates novel hybrid sorbent materials based on ionic liquid (IL) modified porous silica for CO₂ capture, aiming to tackle the limitations of the high viscosity of ionic liquids and to improve the selectivity of porous materials. Phosphonium based ionic liquids were covalently attached onto the surface of bare silica. CO₂ adsorption isotherms at 273 K were used to characterize the porous structures. The adsorption and desorption behavior of CO₂ (at 298, 313 and 333 K) and N₂ (at 313 K) up to 2 bar was measured using a gravimetric method. The grafting of ILs on the support surface causes a loss of microporosity, resulting in a slight decrease in CO₂ adsorption capacity. CO₂/N₂ selectivity is however enhanced. Adsorption thermodynamic study using the Freundlich equation suggests a physical sorption mechanism. The covalent grafting method provides a good IL retention with gas sorption/desorption cycling. The homogeneous surface diffusion model (HSDM) was used to estimate the diffusivities. The diffusion coefficients of CO₂ in the hybrid adsorbents are level with that of unmodified silica at a level of 10⁻⁷–10⁻⁸ m² s⁻¹ and are about two to three orders of magnitude higher than that of neat phosphonium IL. For these IL modified silica, the gas adsorption behavior is dominated by the porous nature of the silica. The IL phases act as a selecting film which notably improves the CO₂ sorption selectivity at a marginal expense of CO₂ sorption capacity and diffusivity.

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1. Introduction

Ionic liquids (ILs) have shown special properties that make them promising candidates rivaling with conventional amine scrubbing for highly selective CO₂ separation. ILs have been reported to have high CO₂ selectivity against other gases including N₂, CH₄ and H₂, and good physical absorption capacity [1,2]. They have reasonable thermal stability, non-volatility, non-corrosion

and tunable physiochemical properties [3,4]. However, they still have some disadvantages, including the relatively high viscosity which limits the gas adsorption/desorption rate [5,6]. Their relatively high cost also casts a concern for a large quantity of usage at an industry scale.

Solid porous materials offer another solution for CO₂ capture with high energy-efficiency, fast adsorption/desorption rate and low cost. Some existing problems however include low CO₂ adsorption capacities at low pressures and low selectivity against competing components from flue gas [7,8].

To overcome the drawbacks, we grafted IL phase onto the surface of porous solid supports, such as silica, to form novel hybrid sorbents for CO₂ separation. The concept was inspired by Supported IL Phase (SILP) that has been established in the last five

* Corresponding authors. Address: School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou, Jiangsu 221116, PR China. Tel.: +86 516 83884079 (J. Zhu). Tel.: +61 3 9545 8575 (J. Huang).

E-mail addresses: zhujiamei@hotmail.com (J. Zhu), jewel.huang@csiro.au (J. Huang).

years as an innovative method to immobilize metal complex catalysts for catalytic reactions such as CO₂ chemical fixation [9–11]. These novel materials have also been used for heavy metal separation [12,13]. Here we explored the application of SILP in gas purification and separation, expecting benefits of thermal/chemical stability, essentially low volatility and high CO₂ selectivity from IL phase, and exploiting the advantages of the low cost and the fast diffusivity of porous solid materials. Grafting a thin film of ILs onto high-surface porous materials not only enlarges the gas/liquid interface, but also shortens the distance for gas diffusion than in a bulk liquid, thus leading to a fast adsorption/desorption rate. The coated IL layer also performs as a selecting film that allows CO₂ to permeate through to the adsorption sites on the solid materials but impedes other undesirable components such as N₂.

We grafted ILs onto porous silica through covalent grafting method. Several research groups have reported CO₂ adsorption equilibria on immobilized ILs *via* wet impregnation method; i.e., pre-formed ILs were physically attached to solid supports. Examples are silica supported tetrabutylphosphonium amino acid [14] and silica supported N-(3-aminopropyl)aminoethyl tributylphosphonium amino acid salts [15]. In both cases no covalent bonds were formed between support materials and ILs. This method results in IL loss over adsorption/desorption cycles and thus the degradation of the adsorbent performance. It is expected that covalent grafting method will improve IL retention and the stability of the SILP sorbents.

We chose phosphonium ILs (PILs) as the IL phase. In comparison to nitrogen-based ILs, PILs show advantages in many aspects. Firstly, phosphonium salts are generally more thermally stable than ammonium salts, beneficial for high temperature operation [16]. Secondly, compared with imidazolium and pyridinium ILs, PILs do not have acidic proton or aromatic rings, which makes them stable towards nucleophilic and basic conditions [17]. Thirdly, PILs generally have lower densities than water, whereas nitrogen-based ILs generally have higher densities. This is beneficial in IL production involving separation from aqueous layers containing inorganic by-products [18]. In addition, the kinetics of phosphonium salt formation are much faster than those of nitrogen based salts, implying higher productivity and lower cost in industry manufacturing of PILs [19,20].

CO₂ adsorption equilibria and diffusion coefficients for these novel IL-modified sorbents were measured to evaluate their potential for industry application. It has been reported that ILs confined in pore structures demonstrate different ionic packing and self-diffusion from the bulk ILs. Consequently gas diffuses differently in the confined ILs combined with various pore structures, resulting in different gas absorption behavior [21–26]. Understanding the gas sorption behavior in porous solid-supported IL phase and the effect from covalent grafting method would be interesting. In this work, CO₂ and N₂ adsorption and desorption behavior in phosphonium ILs grafted silica were measured and compared with those of a bulk trioctyl (propyl)phosphonium tetrafluoroborate ([P₈₈₈₃][BF₄]) IL and a bare silica. The CO₂ sorption thermodynamic and kinetic properties were analyzed using a classic Freundlich equation and the homogeneous surface diffusion model (HSDM).

2. Experimental

2.1. Materials

Silica particles (0.5–1.5 mm particle size, type A, Qingdao Silica Gel Factory, China) were pretreated at 423 K for 3.5 h before use. The pretreated silica is referred as bare silica in the following text.

The chemical structures of the modified silica and ionic liquids as well as their synthetic procedures are illustrated in Fig. 1. The

alkoxysilyl-modified silica (SiO₂-Si) was prepared *via* direct reaction of bare silica with propyltriethoxysilane (98 %, Fluorochem Ltd., UK) (Fig. 1a). Typically, bare silica was added into anhydrous toluene under nitrogen, and then propyltriethoxysilane was introduced. The mixture was stirred at 363 K for 24 h. The resulting solid was filtered off, then washed with acetone and dried in vacuum oven at 353 K. The IL-modified silica (SiO₂-Si-P₈₈₈₃BF₄) was synthesized by grafting method reported before (Fig. 1b) [27,28]. Firstly, grafting agent was synthesized by a nucleophilic displacement of 3-chloropropyltriethoxysilane (97 %, Beijing Fengtuo Chem Co., Ltd., China) with tri-*n*-octylphosphine (97%, Stream Chemicals) in anhydrous toluene at 383 K for 40 h. The mixture was evaporated and dried at 353 K under vacuum. Then the prepared grafting agent and bare silica were stirred in anhydrous toluene at 363 K for 24 h under a nitrogen atmosphere. It was filtered off, washed with acetone and dried in vacuum at 353 K overnight. Finally, the solid was stirred with sodium tetrafluoroborate in acetonitrile at room temperature for 35 h. The solid was washed with acetonitrile, distilled water and then dried at 353 K overnight under vacuum to form an IL modified silica (SiO₂-Si-P₈₈₈₃BF₄). Tributyl (propyl)phosphonium modified silica (SiO₂-Si-P₄₄₄₃BF₄) was prepared by the same procedures using tri-*n*-butylphosphine. The neat phosphonium IL ([P₈₈₈₃][BF₄]) was formed by the procedures reported before (Fig. 1c) [29]. Briefly the mixture of anhydrous toluene, 1-bromopropane (99%, Chengdu Xiya Chem Co., Ltd., China) and tri-*n*-octylphosphine was stirred at 353 K for 24 h under a nitrogen atmosphere. After being evaporated and dried at 353 K under vacuum was obtained trioctyl(propyl)phosphonium bromide ([P₈₈₈₃][Br]). Then [P₈₈₈₃][Br] was stirred with aqueous solution of NaBF₄ in methanol at room temperature for 25 h. The mixture was then concentrated and washed with water until the aqueous phase did not generate precipitate by AgNO₃ test. The product was then dried in vacuum at 333 K for 10 h. All products obtained were confirmed by FTIR (Fig. 2).

IR(ν_{\max} , cm⁻¹) of SiO₂-Si: 2961, 2932, 2875 cm⁻¹ (C-H, aliphatic); 1179, 1069 cm⁻¹ (Si-O-Si).

IR(ν_{\max} , cm⁻¹) of SiO₂-Si-P₈₈₈₃BF₄ : 2955, 2920, 2850 cm⁻¹ (C-H, aliphatic); 1377 cm⁻¹ (P-C); 1120, 1070 cm⁻¹ (Si-O-Si); 1084 cm⁻¹ (B-F).

IR(ν_{\max} , cm⁻¹) of P₈₈₈₃BF₄: 2956, 2917, 2852 cm⁻¹ (C-H, aliphatic); 1352 cm⁻¹ (P-C); 1055 cm⁻¹ (B-F).

2.2. CO₂ sorption measurement

The adsorption isotherm of CO₂ at 273 K was measured by a Quantachrome Autosorb-1-MP to obtain CO₂ adsorption capacity and porosity information. The porous particles were dried and degassed at 373 K under vacuum for 3 h to remove moisture or other volatile contaminants. CO₂ was then introduced into the chamber as adsorbate to the pressure range from 1.33 × 10⁻¹¹ to 1 bar. Density functional theory (DFT) analysis was used to calculate the pore size distribution (PSD) and the pore structure parameters.

Adsorption and diffusivity experiments were examined by an Intelligent Gravimetric Analyzer (IGA-003, Hiden Isochema Ltd.) as shown in Fig. 3. The adsorption isotherms of CO₂ and N₂ were conducted at 298, 313, 333 K and pressures up to about 2 bar. More detailed information on the apparatus can be referred to Liu et al. [30]. About 50–60 mg of sample was held in a quartz container and sealed in a stainless-steel reactor. Firstly, the sample was degassed at 10⁻⁸ bar and 373 K for 8 h until the weight remained stable for at least 1 h. After the sample weight became constant, the temperature was cooled to the desired adsorption temperature. Subsequently, CO₂ or N₂ was introduced to the set pressure. The weight was monitored with time. The adsorption equilibrium reached when no further weight change was observed. After the

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