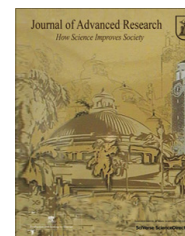




Cairo University
Journal of Advanced Research



ORIGINAL ARTICLE

Efficient and reversible CO₂ capture by amine functionalized-silica gel confined task-specific ionic liquid system

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ARTICLE INFO

Article history:

Received 16 December 2013

Received in revised form 2 February 2014

Accepted 4 February 2014

Available online xxxx

Keywords:

CO₂ absorption

Task-specific ionic liquid

Mesoporous material

Carbon dioxide fixation

ABSTRACT

Simple, efficient and practical CO₂ capture method is reported using task-specific ionic liquid (IL) supported onto the amine-functionalized silica gel. The results have been shown that both the capacity and rate of the CO₂ absorption notably increase in the supported IL/molecular sieve 4 Å system in comparison of homogeneous IL. Additionally, it has shown that the prepared material is capable for reversible carbon dioxide absorption for at least 10 cycles without significant loss of efficiency. The presence of the amine-based IL and the surface bonded amine groups increase the capacity of CO₂ absorption even in a CO₂/CH₄ gas mixture through the formation of ammonium carbamate onto the surface of mesoporous material.

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Introduction

Carbon dioxide (CO₂) is a harmful greenhouse gas with 50–200 years life-time in the atmosphere and made up 84% of U.S. greenhouse gas emission from human activities [1]. Moreover, removal of carbon dioxide from the acidic natural gas (a

gas which contains significant amount of acidic carbon dioxide) is a vital step in the gas sweetening operations [2].

In the past decades, various methods have been proposed for CO₂ capture [3] mainly using ionic liquids (ILs) [4–7]. The term "task-specific" IL refers to non-solvent applications of the IL such as catalysis, synthesis and gas absorption [8,9]. Amine based ILs first reported by Bates et al. [10] and extended with others [11,12] are desirable liquids for carbon dioxide absorption. Despite simple synthetic method and using commercially available starting material, the major drawback of this compound is attributed to half-molar CO₂ uptake per one mol of IL. Moreover, the homogeneous ILs mainly suffer from gas diffusion limitation specially by increasing the viscosity of the CO₂-captured ILs. Recently Wu and co-workers showed that N-(3-aminopropyl) aminoethyl tributylphosphonium amino

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acid based ILs which were supported into the mesoporous silica material had excellent efficiency toward reversible CO₂ capture [13]. Organoamines-grafted on nano-size silica [14] and electrochemical reduction of carbon dioxide are also among the successful and suitable methods reported for CO₂ utilizing [15].

Here, an amine-functionalized mesoporous material which confined by amine based IL is reported for CO₂ absorption/desorption. The aim of modifying the surface with amine precursor is to provide surface amine groups to form ammonium carbamate species with IL after CO₂ uptake. To increase the gas rate and the absorption capacity, molecular sieve 4 Å (which is traditionally used for absorption of carbon dioxide) was added to the system.

Experimental

Preparation of the IL

The IL was prepared according to the known literature procedure [10] with some modifications (Scheme 1a). To a round bottom flask equipped with a condenser, 1-methylimidazole and 2-bromoethylamine hydrobromide were added and the mixture was refluxed in ethanol to form IL 1. After 48 h, the solvent was removed by applying vacuum and the residue was dissolved in minimum amounts of water. The pH of the solution was increased to nearly 8 by adding solid KOH. Then the mixture was slowly filtrated from solid KBr by-product followed by evaporation of the solvent. Then, the resulted IL 2 was dissolved in minimum volume of ethanol to precipitate residual KBr. Subsequent anion exchange of the resulted IL was performed with NaBF₄ in ethanol at room temperature

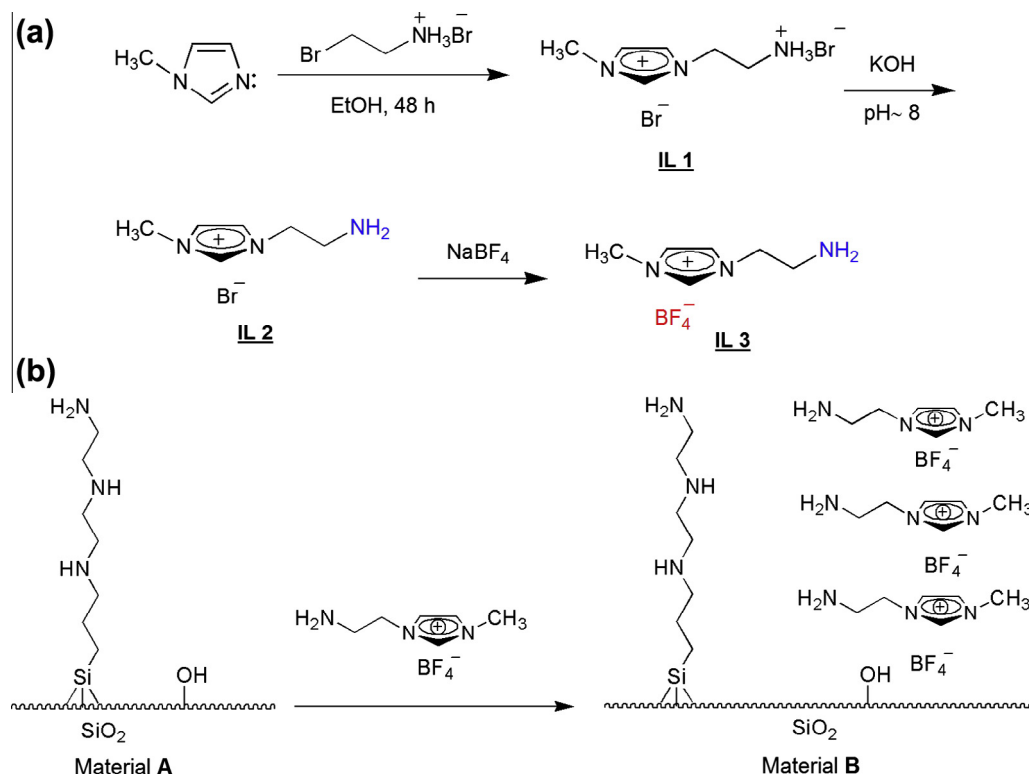
for 24 h (Scheme 1a). IL 3: ¹H NMR 500 MHz D₂O: 3.19 (2H), 3.38 (2H), 3.73 (3H), 4.42 (2H), 7.31 (1H), 7.40 (1H), 8.69 (1H); ¹⁹F NMR 500 MHz D₂O: -148.9. FT-IR (liquid film): 3486, 3145, 3081, 2859, 2066, 1635, 1564, 1464, 1378, 1166 and 1021.

Preparation of the amine-functionalized mesoporous material

Silica gel Davisil™ grade 635 (average pore diameter 60 Å, pore volume 0.75 cm³ g⁻¹, surface area 480 m² g⁻¹) was activated by refluxing in 6 M hydrochloric acid (HCl). After 24 h, the silica gel was washed thoroughly with deionized water to adjust the pH of the solution to 6–7 and dried at 90 °C before undergoing surface modifications. For a sample reaction, 80 g of the activated silica gel was mixed with 70 mmol (~18 mL) of 2-[2-(3-Trimethoxysilylpropylamino)ethylamino]ethylamine in dry toluene. The mixture was heated at 110 °C for 24 h. Then, the solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhlet) and then dried in an oven at 90 °C to give 92 g of surface-bonded amine groups, material A (Scheme 1b).

Preparation of the silica supported IL (material B)

The IL was supported on the surface of the mesoporous material applying physisorption method [16,17]. Typically, an ethanol solution of the 36 mL (~46.5 g) of IL 3 was added to a mixture of 84.75 g material A and 400 mL ethanol over 1 h. The reaction mixture was stirred for 2 h and then the solvent was removed under reduced pressure to afford material B (Scheme 1b) as a yellow powder (~55 wt.% IL 3/material A).



Scheme 1 Synthesis route to IL 3 (a), schematic illustration of preparing material B by physisorb confinement method (b).

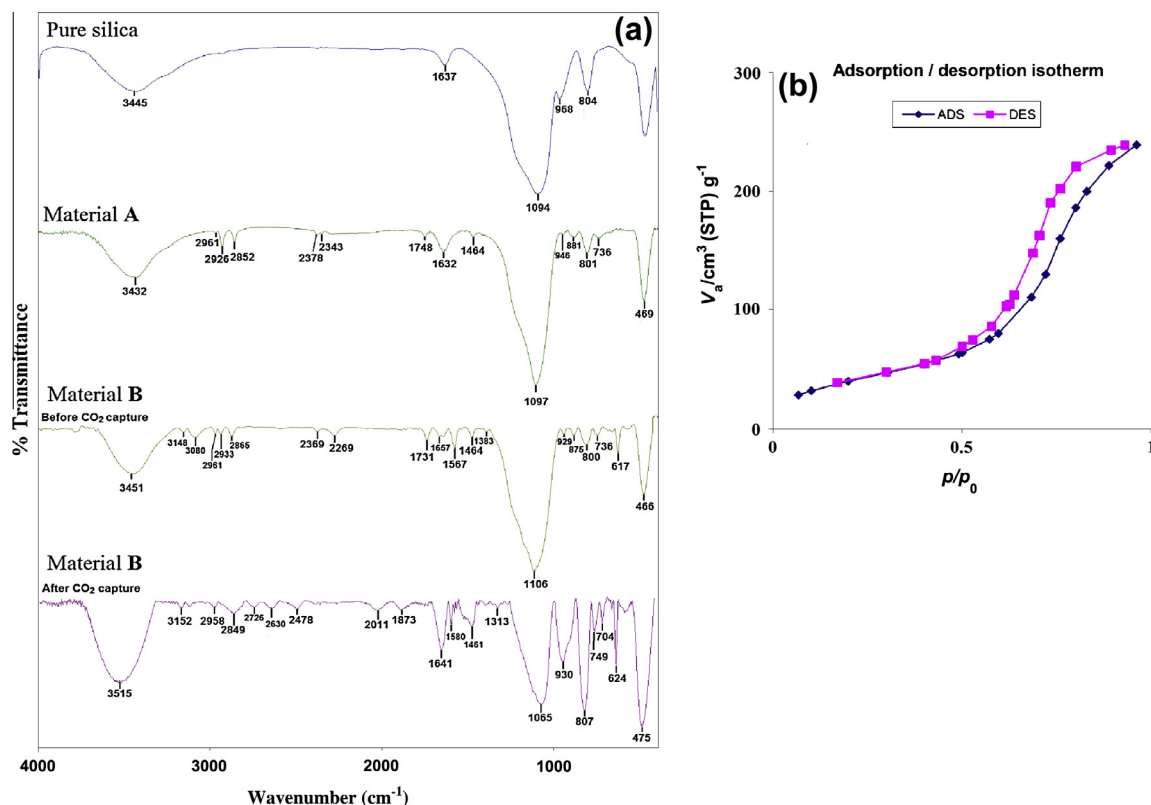


Fig. 1 FT-IR spectroscopy of the pure silica, material **A** and material **B** before and after CO₂ uptake (a) N₂ adsorption/desorption isotherm of the material **B** (b).

Material **B** was dried in oven at 80 °C before gas absorption experiments.

CO₂ uptake experiment of material **B**/molecular sieve 4 Å

CO₂ absorption was carried out in a tube which was filled with a mixture of the material **B** and molecular sieve 4 Å. In this regard, the experiment setup was prepared by mixing 40 g of molecular sieve 4 Å and 20 g of material **B**. Molecular sieve and material **B** were dried before CO₂ treatment. Top and bottom sides of the apparatus are fixed by cotton. Nitrogen was used as an inert gas before carbon dioxide treatment. The purity of CO₂ and N₂ gases was 99.95%. The absorption was carried out at 25 °C for 2 h and at atmosphere pressure with a gas flow rate of 100 ± 5 mL/min. After the absorption experiment, the material was placed at room temperature and pressure to remove physisorbed CO₂ until reaching to a constant weight. Desorption experiments was performed in a rotary evaporator at 45 °C by applying vacuum (100 mbar) and at 85 °C at atmosphere pressure. The amounts of CO₂ were determined with an analytical scale with accuracy of ±0.001 g.

CO₂ uptake experiment of IL **3**

In a typical experiment, 7 g of IL **3** was added to a sample tube. The absorption and desorption experiments were performed according to the identical condition performed for material **B** (see above). Nitrogen was used as an inert gas before CO₂ treatment experiment. Absorption was carried out

at 25 °C for 3 h and at atmosphere pressure with a gas flow rate of 100 ± 5 mL/min. Desorption experiment was performed in rotary evaporator at 45 °C by applying vacuum (100 mbar). During the CO₂ uptake experiment, the mixture of IL **3** was stirred at 600 rpm to provide a homogeneous gas/liquid connection. The changes in the weight of the IL was recorded each 30 min with an analytical scale with accuracy of ±0.001 g.

CO₂ uptake experiment of material **B**/molecular sieve 4 Å from CO₂/CH₄ mixture

The gas preparation system for the CO₂ capture experiment from the CO₂/CH₄ mixture was designed according to the known literature method [18]. In this experiment nitrogen was used as an inert gas before CO₂ treatment. CO₂ and CH₄ were passed from two different valves with the pressure 100 mL/min and then mixed to one line. The absorption experiment was performed according to the method described for material **B**/molecular sieve 4 Å except the uptake time which was performed for 160 min.

Results and discussion

The IL **3** was synthesized by the reaction of 1-methylimidazol and 2-bromoethylamine hydrobromide following anion exchange with NaBF₄ at room temperature (Scheme 1).

Material **A** was easily synthesized by grafting the commercially available amine precursor on the silica surface in the reflux of the toluene. The loading of amine groups was

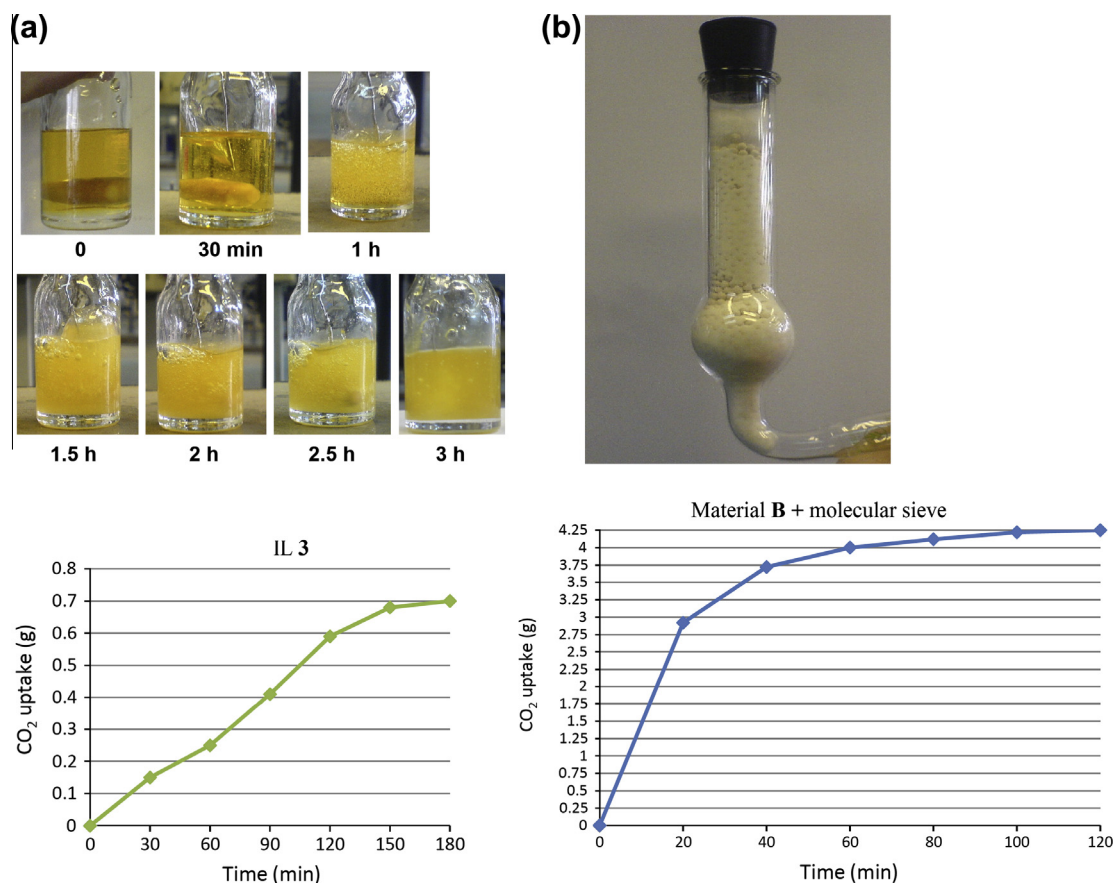


Fig. 2 CO₂ absorption experiment setup and kinetic results for IL 3 (a) and material **B**/molecular sieve system (b).

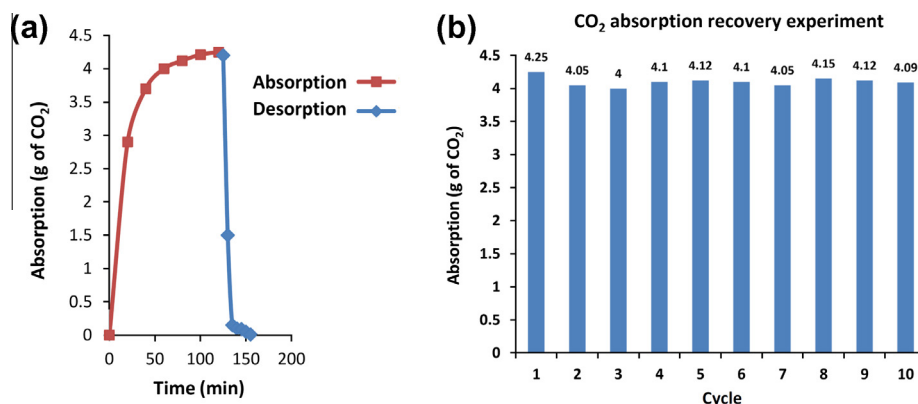


Fig. 3 Results of absorption and desorption experiment (a) recycling results for CO₂ absorption experiment of material **B**/molecular sieve system (b).

calculated from the increasing the weight of the final material **A** to be about 0.5 mmol/g of silica. Material **B** was prepared by impregnation of IL 3 in the form of supported liquid phase (SLP) [16] onto the as-synthesized material **A** (Scheme 1b). In this regard, ethanol solution of the IL 3 was gradually added to a suspension containing fine particles of material **A** and ethanol.

Comparative FT-IR spectra of pure silica, material **A** and material **B** are shown in Fig. 1a. In material **A**, the characteristics bands at 2852 and 2926 cm⁻¹ are attributed to C—H and

N—H stretching frequencies of the surface alkyl amine functionalities. The corresponding bands at 3148, 3180, 2961, 2933 and 2865 cm⁻¹ in material **B** belong to aromatic and aliphatic C—H and aliphatic N—H stretching frequencies of the supported IL 3 in material **B**. It is worth mentioning that the bands observed near the 1464 and 1748 cm⁻¹ in both of material **A** and **B** are attributed to the N—H bending frequencies and C=N aromatic frequencies of imidazolium ring of the supported IL 3.

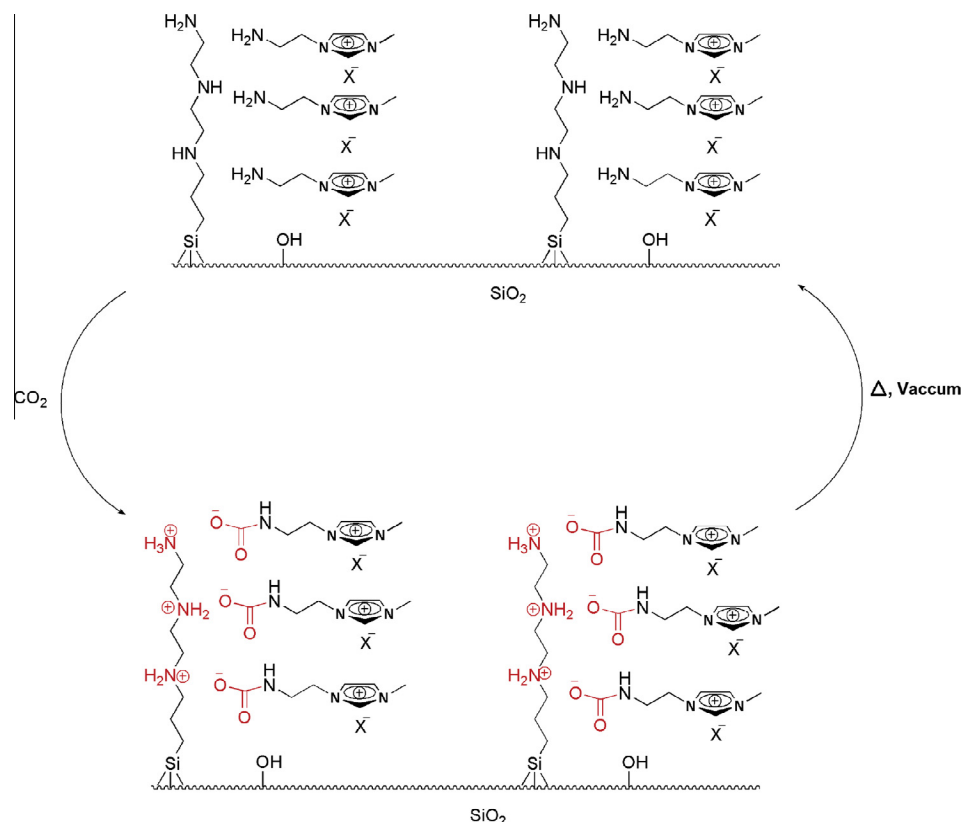


Fig. 4 Proposed mechanism of CO₂ capture with material **B**.

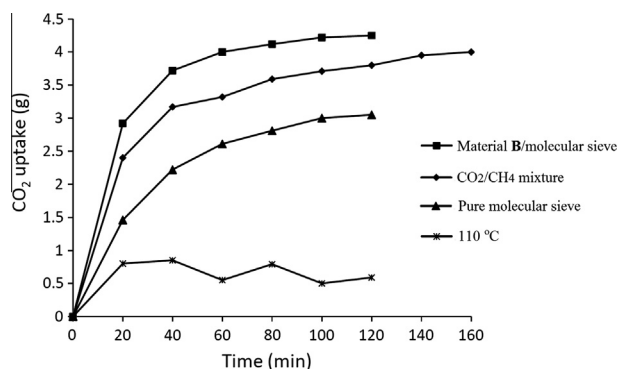


Fig. 5 CO₂ absorption experiment for material **B**/molecular sieve system, CO₂/CH₄ mixture, pure molecular sieve and absorption at 110 °C.

N₂ adsorption/desorption isotherm of the material **B** is shown in the Fig. 1b. BET (Brunauer–Emmett–Teller) surface area of the catalyst was decreased from the initial 480 m² g⁻¹ to 127 m² g⁻¹. Moreover, the pore volume of the material **B** was reduced from the initial 0.75 cm³ g⁻¹ to 0.31 cm³ g⁻¹. The mean pore diameter of the catalyst calculated to be 6.4 nm derived from the BJH (Barrett–Joyner–Halenda) average pore diameter analysis. The decrease in surface area and the pore volumes in the N₂ adsorption–desorption analysis of the material **B** were clearly prove that the IL **3** was supported onto the channels of the mesoporous material **A**.

Before the carbon dioxide uptake experiment, material **B** and molecular sieve was dried in an oven to remove any residual water and ethanol which was used during the material preparations. The color of the resulted material is pale yellow and cannot be easily differentiated by sight.

To enhance the absorption rate and capacity of the system, material **B** (20 g) was mixed with molecular sieve 4 Å (40 g). This allows increasing the experiment gas flow rate to 100 mL/min and decreasing the experiment time. The other end of the absorbent apparatus was conducted to a ventilation system to pass out carbon dioxide out of the lap space. It is worth mentioning that the molecular sieve 4 Å is a commercially available material which can specifically absorb small molecules such as CO₂ and NH₃.

The amount of carbon dioxide uptake was determined according to the reported literature method [16] using analytical balance with accuracy of ±0.001 g. To provide a kinetic comparison, CO₂ absorption was also performed for pure IL. In this regard, 7 g of IL **3** (equal to its amount which was used for preparation of 20 g material **B**) was added to a sample tube and the liquid was treated with the flow of carbon dioxide. The experiment setup and kinetic results of IL **3** and material **B**/molecular sieve system are shown in Fig. 2.

The result suggested that the amount of CO₂ absorption reaches near to the theoretical value after 3 h. The viscosity of the IL **3** in homogeneous CO₂ capture experiment was increased during the CO₂ treatment which this factor usually causes some technical problem. However, in the case of material **B**/molecular sieve system, only after 1 h the system absorb more than 94% of its final absorption capacity.

The weight changes in material **B**/molecular sieve was recorded every 20 min. In this regard for each step, the gas flow is terminated and the apparatus was placed at room temperature to remove physisorbed carbon dioxide. When the mass of the material reached to a constant value, it was recorded. The results show that the presented system absorbs 4.25 g carbon dioxide after 2 h treatment. The results of absorption-desorption experiments and recycling of the material **B**/molecular sieve for CO₂ uptake are shown in Fig. 3.

For desorption experiment, the apparatus constituent was transferred to a round bottom flask of a rotary evaporator system by applying vacuum (100 mbar) and 45 °C for 30 min. Every 5 min the sample was weighted and the data were recorded. The results suggested that the presented CO₂ absorption system can easily release the carbon dioxide under mild temperature condition after 30 min. Desorption experiment was also performed at atmospheric pressure to explore the role of the applied vacuum. It is found that the lowest temperature to perform efficient desorption for 30 min is 85 °C. This observation clearly indicates that applying the vacuum is necessary to perform efficient desorption at mild thermal condition. To investigate the recyclability of the material, the recovered material **B**/molecular sieve 4 Å was subjected to another carbon dioxide absorption experiment. It was shown that the absorbent can be reused for at least 10 cycles without noticeable loss of efficiency (Fig. 3b).

Worthy to note that the both of the surface-bonded amine groups and IL **3** are capable to interact with carbon dioxide. This fact proposed a synergetic effect between IL **3** and the surface grafted amine which can increase the CO₂ capture capacity. In this regard, it is proposed that the absorption mechanism comprises formation the ammonium carbamate onto the surface of the mesoporous material after CO₂ uptake (Fig. 4).

FT-IR analysis of material **B** before and after CO₂ absorption is shown in Fig. 1a. A new and characteristic band which was observed at 1641 cm⁻¹ is attributed to C=O stretching frequency of carbamate moiety of the surface bonded ammonium carbamate. This observation proves the hypothesis of forming ammonium carbamate in the material **B**.

Separation of CO₂ from a mixture of gases such as CO₂/CH₄ is an important issue since CH₄ is a valuable source of energy. In the sour gas, CO₂ participate as an impurity which directly decrease the heat capacity of methane (CH₄). Our attempts for separation CO₂ from a mixture of CO₂/CH₄ showed that the applied system for carbon dioxide absorption can also capture CO₂ from the CO₂/CH₄ mixture with slightly longer time (Fig. 5). To study the effect of pure molecular sieve, 40 g of this absorbent was treated for carbon dioxide capture. The results show that the rate and the capacity of molecular sieve 4 Å are smaller than those of material **B**/molecular sieve 4 Å system. A gap of CO₂ uptake capacity (~1.2 g) which exists between molecular sieve and material **B**/molecular sieve system (see Fig. 5) is attributed to the amount of CO₂ absorbing of 20 g of material **B**. Our attempts to perform CO₂ capture at elevated temperature did not lead to a desirable result (Fig. 5). A plausible explanation to interpret significantly lower absorption may be due the fact that at high temperature absorption-desorption phenomena simultaneously occur and the material is not capable to retain the captured carbon dioxide.

Conclusions

In summary, a new amine based IL confined onto the mesoporous material modified with amine group was designed for reversible CO₂ absorption. The results showed that combination of molecular sieve with material **B**, notably increase the rate and the amounts of CO₂ absorption even for CH₄/CO₂ gas mixture. All the material was synthesized with commercially available starting material. The measurements showed that the rate and kinetic of CO₂ absorption of the supported IL system were much higher than those of the pure IL **3**. Moreover, no special precaution is need for this system in comparison with homogeneous IL. It is believed that the presented method is a good candidate to replace the traditional absorbent methods even for large-scale CO₂ capture applications.

Conflict of interest

The authors have declared no conflict of interest.

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