Immobilization of amino acid ionic liquids into nanoporous microspheres as robust sorbents for CO₂ capture†

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Supported nanoporous microspheres immobilized with amino acid ionic liquids (AAILs) as robust sorbents were developed for CO₂ capture. AAILs could be facilely immobilized into porous support materials. The developed sorbents exhibited fast kinetics as well as good sorption capacity, and can be regenerated and reused. The presented strategy may pave the way for developing AAIL-functionalized sorbents with high capacity and fast CO₂ transport kinetics.

Excessive CO₂ emission resulting from combustion of fossil fuel is a major anthropogenic factor in global warming.1–4 One promising solution to reduce CO₂ emission from large emission sources (e.g. coal fired power plants) is to capture the generated CO₂ with sorbents before it is emitted in the atmosphere.5,6 The predominant commercial CO₂ capture approach using aqueous amine scrubbing towards ammonium carbamate formation has some inherent disadvantages. These include relatively high amine loss and degradation, high energy consumption for regeneration, and unavoidable equipment corrosion.7–9 Therefore, novel robust sorbent materials and technologies for efficient and economical CO₂ capture have attracted increasing attention from both academia and industry.

To overcome the above-mentioned drawbacks of aqueous amine solutions, ionic liquids (ILs) are considered to be attractive alternatives for the uptake of CO₂ because of their negligible vapor pressures, high thermal stability, and tunable physicochemical properties.10–12 Many research groups, especially that of Brennecke,13,14 have carried out significant research on the solubility of CO₂ in imidazolium-based ILs. In general, the absorption of CO₂ by these traditional ILs had to be performed under very high pressure and very long time for equilibrium to be reached,15 which is not sufficient for practical CO₂ capture. Introduction of special groups to ILs to achieve more rapid and efficient absorption of CO₂ in ILs is possible.16–18 Bates and co-workers developed a task-specific ionic liquid (TSIL) for CO₂ capture by introducing an amine group to the cation of ILs and found that the CO₂ uptake approached 0.5 mol mol⁻¹ IL under normal pressure and temperature.5 After that, a number of amine-functionalized ILs have been explored for CO₂ capture.19–21 Among them, Fuku­moto et al.22 first reported the preparation of amino acid-based ILs (AAILs) from 20 natural amino acids in 2005. Since then, AAs have been used to act as a platform for the preparation of functionalized ILs and thus CO₂ sorbents or membranes.12,15,21–26 For example, Zhang et al.27 reported that (3-aminopropyl)tributylphosphonium amino acid salts ([AIP4443][AA]) could approach high CO₂ uptake within 80 min. Jiang et al.12 have successfully synthesized tetraalkylammonium-based AAILs which presented improved reaction and mass transfer rates of CO₂ in the ILs.

Although the CO₂ absorption in AAILs is substantially improved, the relatively high viscosity of ILs results in low sorption and desorption rates and might limit their eventual use in large-scale CO₂ gas removal.7,13,18,22 Immobilization of AAILs into porous inorganic supports is believed to be a promising strategy to prepare robust sorbents for CO₂ removal.7 Herein, we conducted a proof-of-concept study showing that robust sorbents can be prepared through immobilization of 1-ethyl-3-methylimidazolium amino acid salts ([EMIM][AA]) into nanoporous poly(methylmethacrylate) (PMMA) microspheres. We developed supported AAIL sorbents with minimal CO₂ diffusion resistance and good capacity. AAILs ([EMIM][glycine (Gly)], [EMIM][alanine (Ala)], and [EMIM][arginine (Arg)]) were prepared using a neutralization method reported previously.28 In brief, the [EMIM][OH] solution prepared through anion exchange from the [EMIM][bromide (Br)] solution was added in slight excess of an equimolar AA (i.e.
respectively. The CO₂ uptake by [EMIM][Gly] and [EMIM][Ala] within 45 min for [EMIM][Gly], [EMIM][Ala], and [EMIM][Arg], prepared using the impregnation ported [EMIM][AA] in nanoporous PMMA microspheres, to the high CO₂ diffusion capacity of liquid [EMIM][AA] (Fig. S3†). The liquid [EMIM][AA] was spread in a thermogravimetric analysis (TGA) microbalance quartz sample cell, heated to 105 °C in the N₂ atmosphere and then adjusted to 40 °C to measure the CO₂ uptake. As illustrated in Fig. S3†, the sorption rate of liquid [EMIM][AA] (~35 mg) was very slow due to the high CO₂ diffusion resistance caused by the high viscosity of ILs. The capacity of the three liquid [EMIM][AA]s (~35 mg) was less than 0.2 mmol g⁻¹ within 45 min. When the amount of [EMIM][AA] placed in the TGA sample cell was reduced to 7 mg, which allowed [EMIM][AA] to be effectively spread in the sample cell, the sorption rate was significantly enhanced and reached a sorption capacity of 0.47, 0.45, and 0.09 mmol CO₂ per g solvent within 45 min for [EMIM][Gly], [EMIM][Ala], and [EMIM][Arg], respectively. The CO₂ uptake by [EMIM][Gly] and [EMIM][Ala] AAIL (Table S1†) was comparable to those of standard seques-tering amines such as monoethanolamine (MEA) and disopropanolamine (DIPA).³

To enhance the sorption rate, adsorption of CO₂ by supported [EMIM][AA] in nanoporous PMMA microspheres, prepared using the impregnation–vaporization method,⁶,²⁷,²⁸ was studied. Fig. 1 presents the typical scanning electron microscopy (SEM) images of as-prepared [EMIM][AA]–PMMA sorbents, indicating that the resultant sorbents had a uniform diameter of about 500 μm. The high-magnification SEM image (Fig. 1b) clearly shows that the surface of the PMMA microsphere featured a hierarchical roughness and nanotexture. By closely observing the cross-section of the sorbents (Fig. 1c), it can be seen that the interior of the microspheres retained a highly porous structure (Fig. 1d). These observations led us to conclude that the versatile nanoporous structure of [EMIM][AA]-

Scheme 1 Schematic diagram of synthesis and immobilization of functional [EMIM][AA] for CO₂ capture.

Fig. 1 Typical SEM images of as-prepared [EMIM][AA]–PMMA sorbents. (a and b) Surface structures; (c and d) cross-section structures.

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Fig. 2 CO₂ adsorption/desorption of three different sorbents [EMIM][AA]–PMMA (with an [EMIM][AA] loading of 50 wt% in the sorbents). The inset shows the photo-image of as-prepared [EMIM][AA]–PMMA sorbents.
sorbent, respectively. In addition, the process of CO₂ uptake in our AAIL sorbents is reversible and [EMIM][AA]-based sorbents could be regenerated by exposing them to flowing N₂ at 105 °C for 60 min (Fig. 2), indicating their practical use as solid sorbents for CO₂ removal. It is worth noting that the desorption was fast in the beginning but slow toward the end, similar to the phenomenon reported in other sorbents.⁶⁻¹⁰

The enhanced sorption properties of [EMIM][AA]-PMMA sorbents led us to explore their CO₂ sorption mechanism. For amino-functionalized TSILs, both 1 : 1 and 1 : 2 reaction stoichiometry mechanisms were proposed.¹⁰ Gurkan et al.¹¹ argued that anion-functionalized ILs (i.e. trihexyl(tetradecyl)phosphonium amino acid or [P₆₆₆₁₄][AA]) can react with CO₂ in a 1 : 1 stoichiometry, i.e. only forming carbamic acid but not carbamate. The 1 : 1 stoichiometry theory works with [P₆₆₆₁₄][AA] ILs but fails in other anion-functionalized ILs (e.g. tetraethylammonium amino acid or [N₂₂₂₂][AA]).¹₂ tetrabutylphosphonium amino acid or [P(C₄)₄][AA] and 1-n-butyl-3-methylimidazolium amino acid or [C₄MIM][AA]). For ILs with large-sized ion pairs (e.g. [P₆₆₆₁₄][AA]), it is difficult for two amino groups to approach each other so that only carbamic acid is formed according to 1 : 1 stoichiometry.¹³ When the ion pair size of ILs is small, the formed carbamic acid can approach and further react with another amino group to form a neutral carbamate in 1 : 2 stoichiometry.¹⁴¹⁵ The capture mechanism of CO₂ in our developed [EMIM]-[AA] solvents and sorbents is believed to be similar to that of [C₄MIM][AA], i.e. one CO₂ molecule interacts with two amino groups (1 : 2 stoichiometry):

The experimental CO₂ sorption capacities of [EMIM][Gly] and [EMIM][Ala] approached 0.5 mol mol⁻¹ AAIL, their theoretical maximum value for CO₂ capture (Table S1†). It is noteworthy that the experimental CO₂ sorption capacity of [EMIM][Arg]-sorbents and sorbents is believed to be similar to that of [C₄MIM][AA], i.e. one CO₂ molecule interacts with two amino groups (1 : 2 stoichiometry):

![CO₂ capture mechanism](image)

of the sorbents leading to reduced capacity. The CO₂ adsorption of [EMIM][Gly]–PMMA sorbents with various [EMIM][Gly] loadings (0 or PMMA, 20, 40, 50, 60, and 100 wt%) is in the sorbents at 40 °C. The inset shows the CO₂ capacity vs. [EMIM][Gly] loading in sorbents.

Fig. 3 CO₂ adsorption of [EMIM][Gly]–PMMA sorbents with various [EMIM][Gly] loadings, shown in Fig. S6,† exhibited similar trends.

Fig. 4 presents the effects of sorption temperature on CO₂ uptake properties. It can be seen that the CO₂ capture capacity decreased almost linearly with increasing temperature, with the highest (1.71 mmol per g sorbent) and lowest capacities (1.02 mmol per g sorbent) at sorption temperatures of 25 and 80 °C, respectively. This is because the interaction between a sorbent and a sorbate is weakened as the temperature increases. It is noteworthy to point out that our [EMIM][Gly]-based sorbents possess higher capacity (Fig. 4) at 80 °C than that (0.86 mmol per g sorbent) of activated carbon-supported tertiary amide sorbents at 29 °C.²⁴ The estimated activation energy of CO₂ adsorption in [EMIM][Gly] (50 wt%)–PMMA sorbent was approximately 6.8 kJ mol⁻¹.

Multiple cycle tests of [EMIM][Gly]–PMMA sorbents were conducted and are presented in Fig. 5. No obvious changes of sorption rate were observed. A small decrease in adsorption capacity was seen and might be attributed to a possible incomplete desorption during regeneration. The adsorption and desorption operations were completed in 40 and 60 min, respectively, and about 1.5 mmol CO₂ was captured per gram sorbent in each cycle. Fourier transform infrared spectroscopy (FTIR) experiments showed no obvious chemical degradation in [EMIM][Gly]–PMMA sorbents during multiple cycles (Fig. S7†).

In summary, three [EMIM][AA]-type AAILs were synthesized and immobilized into nanoporous PMMA microspheres for CO₂ removal. The developed AAILs could be facilely immobilized into nanoporous microparticles with various loadings. More significantly, the sorbent retained the highly porous structures after AAIL loading and exhibited fast kinetics as well as reasonably high sorption capacity and could be easily regenerated and reused. When exposed to CO₂ at 40 °C, [EMIM][Gly]–PMMA sorbents achieved the highest CO₂ capture capacity (1.53 mmol per g sorbent or 0.49 mol mol⁻¹ AAIL) compared with the other two sorbents, following the 1 : 2 stoichiometry
theory. In addition, the CO₂ uptake performance of the resultant sorbents indicated that the adsorption properties of AAIL sorbents could be finely tuned via sorbent structure, AAIL loading, and sorption temperature. The presented pathway may pave the way for developing similar AAIL functionalized sorbents with high capacity and fast CO₂ transport kinetics.

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Notes and references