

Development of amino acid and amino acid-complex based solid sorbents for CO₂ capture



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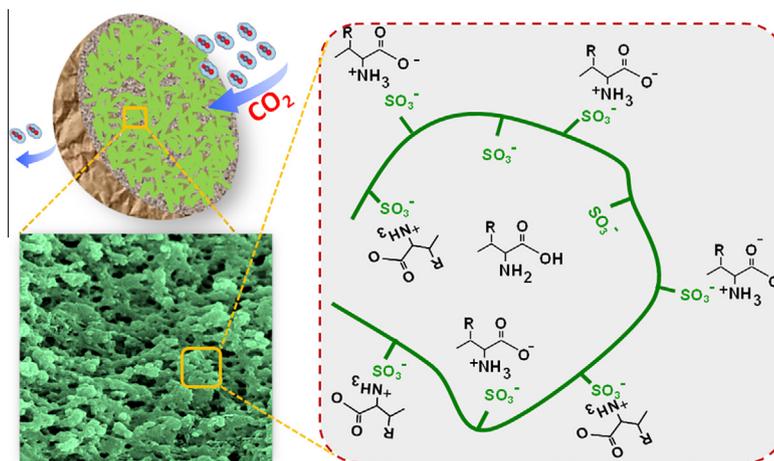
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HIGHLIGHTS

- Innovative amino acid (AA) and AA-complex based solid sorbents were developed for CO₂ capture.
- Complexed AA had improved AA water solubility and higher CO₂ adsorption capacity.
- The factors affecting CO₂ adsorption properties were investigated.
- AA sorbents could eliminate corrosion concerns and retain AA's unique properties.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, amino acid (AA) and AA-complex based solid sorbents for CO₂ removal were investigated by immobilizing AAs and AA-complexes into porous polymethylmethacrylate (PMMA) microspheres. Deposition of pure AAs into porous PMMA supports led to limited CO₂ adsorption in sorbents, because large AA particles or crystals were formed during deposition of pure AAs into PMMA microspheres and some pores of the PMMA microspheres were clogged. Among the AA sorbents studied, Arginine (Arg) solid sorbents had the highest CO₂ adsorption capacity. Interestingly, by forming AA-complexes with other polymers, we substantially improved AA water solubility, achieved uniform immobilization of AAs inside PMMA microspheres, and obtained high CO₂ adsorption capacity. We found that the types of AA-complexes, complex loading capacity, and ratio of AAs in the complexes could have significant effects on CO₂ adsorption properties. Especially, complexing Arg with a strong polyelectrolyte (i.e. polystyrene sulfonate) resulted in substantially improved AA water solubility and high CO₂ adsorption capacity. Our developed AA-complex based solid sorbents could be innovative since they could eliminate concerns related to potential equipment corrosion as well as high heat duty associated with aqueous solvent regeneration all the while retaining the advantageous properties (high thermal stability, excellent biocompatibility, and negligible volatility) of AAs.

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1. Introduction

Due to the possible relationship between anthropogenic CO₂ and global warming, CO₂ capture from power plants has attracted more and more interest [1–6]. Among the current capture technologies including solvents, membranes, and solid sorbents, amine scrubbing using aqueous amine solutions has been used on a small scale in industry for CO₂ capture [2,7–10]. Alkanolamines such as monoethanolamine (MEA), diethanolamine, and N-methyldiethanolamine have been extensively studied as adsorbents to selectively capture CO₂ [11–13]. Although these alkanolamines seem to present many advantages, they suffer from some inherent shortcomings including amine loss and degradation, high absorbent regeneration energy, and corrosiveness to equipment [14–16]. Additionally, these organic solvents are highly toxic and volatile and, as such, they are not environmentally friendly [17]. Ionic liquids (ILs) have attracted much attention as green solvents because of their extremely low vapor pressures, high thermal and chemical stability, and tunable physicochemical properties [17–20]. However, commercial ILs are expensive and their preparation processes are complicated [17,21]. Recently, aqueous alkaline salts of amino acids (AAs) have been evaluated as alternatives for alkanolamines and ILs for CO₂ removal [22–27]. Compared to the traditional amines (e.g. MEA), AAs present a number of advantages such as superior thermal stability, excellent biocompatibility, and negligible volatility [21,26]. Meanwhile, AA salt solutions have similar or even greater CO₂ capacity compared to MEA; and AAs are much cheaper than ILs and can be produced in large quantities [28].

However, current amine solvent systems require intensive regeneration energy and present problems such as equipment corrosion and foaming issues [3]. By contrast, solid sorbents are believed to be able to eliminate corrosion problems and substantially reduce energy requirements (e.g. a reduction of 30–50%) for regeneration than the current MEA-based CO₂ scrubbing process [1,14,29–33]. The physisorption of CO₂ on porous adsorbents, such as zeolites, silica gels, porous aluminas, activated carbons, and metal–organic frameworks, has been extensively investigated [34–39]. Unfortunately, CO₂ capture based on these porous adsorbents suffers from low selectivity and water tolerance [16,29]. Grafting of amine functionalities onto porous solid supports with a high surface area would combine the attractive features of solvent systems with solid sorbents [40,41]. Therefore, many types of amine functionalities, such as polyethyleneimine and task-specific ionic liquids, have been immobilized into porous support materials for CO₂ removal [42–49].

In order to take advantage of the strengths of both solid sorbents and AAs, in this contribution, we demonstrated the feasibility of developing, for the first time, AA and AA-complex based sorbents as new types of solid sorbents for CO₂ removal.

2. Materials and methods

2.1. Material

Arginine (Arg), Arginine ethyl ester (AEE), ornithine (Orn), histidine (His), aspartic acid (Asp), hexadecyl trimethyl ammonium bromide (HTAB), Span 20 (S-20), sodium dodecyl sulfate (SDS), polystyrene sulfonate (PSS, $M_w = 70,000$), and MEA were purchased from Sigma Aldrich Co. (St. Louis, MO). Polymethylmethacrylate (PMMA) microspheres with a specific surface area of 470 m²/g were purchased from Supelco Co. (Bellefonte, PA).

2.2. Characterization of AAs and AA-complexes

AA and AA-complex solutions were prepared by dissolving AA or AA-complex in deionized water. Solubility of AAs and AA-complexes

was examined. AA or AA-complex of a specific amount was added to deionized water followed by vortexing. Particles remained undissolved were weighed and solubility was calculated by dividing the amount of AA dissolved by the volume of water. Zeta potential and colloidal size of Arg, PSS, and Arg/PSS complexes were determined using a Zetasizer 2000 (Malvern, Westborough, MA). Particles formed upon freeze-drying were examined using scanning electron microscopy or SEM (Hitachi S-4700, Tokyo, Japan).

2.3. Preparation of AA and AA-complex based solid sorbents

Arg, AEE, Orn, His, and Asp were investigated in this study to develop AA based sorbents; Asp was selected as a representative of negatively-charged AAs and the other AAs had good CO₂ absorption capacities when used as solvents [22]. A well-studied physical immobilization method was applied to prepare AA and AA-complex based solid sorbents. Similar to our previous studies [14,31], 400 mg of PMMA microspheres was first mixed thoroughly in a glass vessel with an AA or AA-complex solution (see Supporting information, Fig. S1). Next, the mixed solution was placed in a rotary evaporator (IKA, Wilmington, NC) using a stirring rate of 100 rpm with vacuum applied for 30 min. The suspension solution was then heated until boiling under vacuum and kept heating until water was completely evaporated. The resultant AA-impregnated PMMA (designated as AA-PMMA, e.g. Arg-PMMA) sorbents or AA-complex-impregnated PMMA (designated as AA-complex-PMMA, e.g. Arg/PSS-PMMA) sorbents were collected and placed in a vacuum oven at 120 °C overnight and subsequently stored.

2.4. Characterization of AA and AA-complex based solid sorbents

The morphologies of AA and AA-complex based PMMA solid sorbents were examined using SEM. PMMA sorbent microspheres were cut in half or into pieces using a thin sharp blade under optical microscopy; broken microspheres and whole PMMA sorbent microspheres were mounted onto stainless steel supports and gold-sputtered. The surfaces of the broken microspheres (cross-section) and whole PMMA sorbent microspheres were imaged.

The adsorption and desorption performance of AA and AA-complex based PMMA solid sorbents was determined using thermogravimetric analysis (TGA) (Perkin Elmer, Waltham, MA). Similar to our previous protocols [14,31], approximately 20 mg of the PMMA sorbents was placed in the TGA microbalance quartz sample cell filled with flowing N₂ gas (100%), heated to 105 °C by 20 °C/min, and kept at 105 °C for ~60 min until no weight loss was observed. The temperature was then decreased by 20 °C/min to 40 °C, at which point 100% dry CO₂ was introduced for CO₂ adsorption. When no obvious weight gain was observed, the gas was switched to pure N₂ to desorb CO₂ via pressure-swing. The desorption cycle was terminated when no obvious weight loss was noticed. The flow rates of N₂ and CO₂ were 200 ml/min. The weight gain and loss of the PMMA sorbent microspheres were recorded. The CO₂ adsorption capacity in mol·CO₂/(kg sorbent) was calculated from the weight change of the samples during the adsorption process.

3. Results and discussion

In this study, AA solid sorbents were first developed by mixing PMMA microspheres with aqueous AA solutions followed by evaporation of the solvent (see Supporting information, Fig. S1). AAs were selected as adsorption materials because they have superior thermal stability, excellent biocompatibility, negligible volatility, and excellent CO₂ absorption capacity as solvents [22–27,50]. Nanoporous PMMA microspheres were chosen as the support

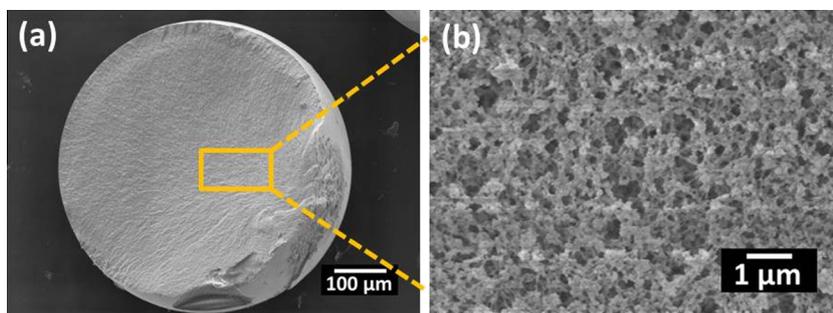


Fig. 1. Typical SEM images of (a) cross-section and (b) higher magnification of PMMA microspheres.

material, because they possess large specific surface area (BET surface area of $470 \text{ m}^2/\text{g}$) and a hierarchical structure of multi-scaled pores, which are beneficial for the development of amine based solid sorbents. As shown in Fig. 1, the PMMA microspheres have an interconnected porous network within the PMMA framework which can facilitate CO_2 diffusion.

The CO_2 adsorption properties of AA solid sorbents were examined and a few AAs (i.e. Arg, His, Orn, Asp, and AEE) were examined (Fig. 2). In general, the amino groups of AAs that are immobilized in PMMA microspheres can react with CO_2 molecules thereby capturing CO_2 and producing ammonium carbamates under anhydrous conditions [16,30]. We found that Arg-, His-, and Orn-PMMA sorbents (AA loading of 20 wt.%) presented low CO_2 adsorption capacity with capacities of $0.5 \text{ mol-CO}_2/(\text{kg sorbent})$ for Arg-PMMA sorbent, $0.2 \text{ mol-CO}_2/(\text{kg sorbent})$ for His- and Orn-PMMA sorbents, and $0.1 \text{ mol-CO}_2/(\text{kg sorbent})$ for Asp- and AEE-PMMA sorbents. We next examined the effect of Arg loading in Arg-PMMA sorbents on CO_2 adsorption capacity. Fig. 3 shows the CO_2 adsorption capacity at 40°C of the sorbents with various Arg loadings. The CO_2 adsorption capacity increased with increasing Arg loading and achieved a maximum adsorption capacity of $0.5 \text{ mol-CO}_2/(\text{kg sorbent})$ at 20 wt.% of Arg. Further increasing Arg loading to 40 and 50 wt.%, the CO_2 adsorption capacity decreased dramatically. Therefore, the adsorption capacity of pure AA immobilized solid sorbents was low overall.

The SEM images shown in Fig. 4 could explain the low capacity of PMMA sorbents immobilized with pure AAs. PMMA microspheres exhibited a porous structure (Fig. 4b); however, the distribution of AAs within the PMMA microspheres was non-uniform. More problematically, large AA particles or crystals (Fig. 4a, inset) formed inside and outside the PMMA microspheres during sorbent preparation (Fig. 4) and some pores of the PMMA microspheres

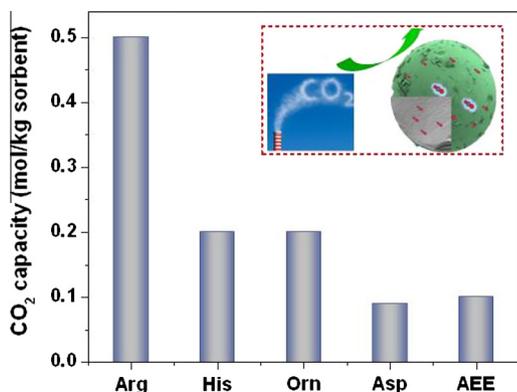


Fig. 2. CO_2 adsorption capacity of AA-PMMA sorbents. The content of AAs in the sorbents was 20 wt.%. Inset shows a schematic illustration of AAs inside PMMA microspheres and their CO_2 capture process.

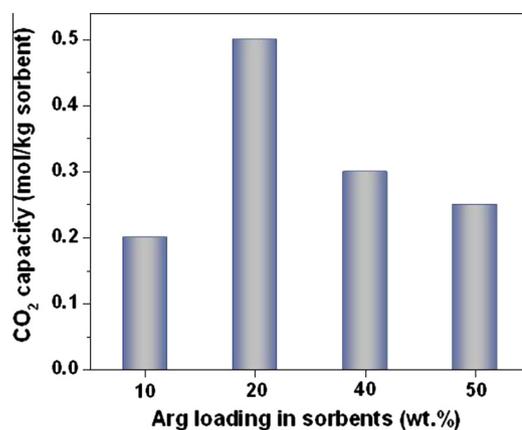


Fig. 3. CO_2 adsorption capacity of Arg-PMMA sorbents vs. Arg loading.

were clogged (Fig. 4b). The formation of large AA particles or crystals could probably be attributed to the low water solubility of AAs; for instance, the solubility of Arg was about 0.06 g/ml (Table 1). Moreover, during CO_2 adsorption, salt bridges or hydrogen-bonded networks of amine- CO_2 zwitterions may form and may inhibit further diffusion of CO_2 from the surface into the interior of PMMA microspheres [29,51,52] thereby leading to low utilization of Arg molecules. The decrease in CO_2 adsorption capacity with increasing Arg loading (Fig. 3) most likely was also due to the “overloading” of Arg, which resulted in the blockage of PMMA pores and a decrease in accessible gas-Arg interface areas [29,53].

Since AA solid sorbents had low CO_2 adsorption capacity, they probably would not be feasible for practical industrial CO_2 removal. In order to improve their CO_2 adsorption capacity, efforts were devoted to inhibiting the formation of large AA particles or crystals, which leads to low surface area, during sorbent formation. Among the AAs studied, Arg exhibited the highest CO_2 adsorption capacity (due to its multiple amino groups) and thus was selected for such efforts. Our strategy was to form AA-complexes with a variety of surfactants or polymers (e.g. HTAB, S-20, SDS, and PSS). Table 1 presents the water solubility of Arg before and after complex formation. We found that the introduction of HTAB, S-20, and SDS led to a mild increase while PSS resulted in a substantial increase in water solubility. After being complexed with PSS at an Arg/PSS monomer molar ratio of 1:1, the solubility of Arg (0.3 g/ml) was fivefold of that of pure Arg. The solubility of Arg further increased with a decreasing molar ratio of Arg to PSS monomer and, compared to pure Arg, approximately 10-fold solubility (0.5 g/ml) was achieved at the Arg/PSS monomer molar ratio of 1:2 (Table 1). The size and zeta potential values of formed Arg/PSS complexes were examined. As shown in Fig. 5, Arg was positively charged and PSS negatively charged with zeta potential values of $+10$ and -40 mV , respectively. Upon complexing, the Arg/PSS complexes

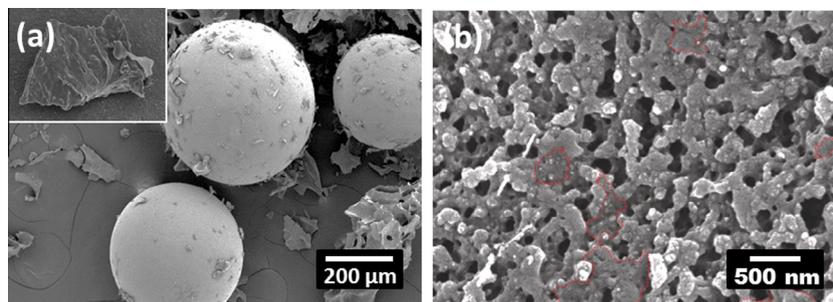


Fig. 4. SEM images of (a) as-developed Arg-PMMA sorbents and (b) their inside microstructure. Inset (a) shows a typical large Arg particle or crystal formed on the surface of Arg-PMMA sorbents. Highlighted (dotted red lines) areas in (b) indicate AA-rich areas that clogged some pores within Arg-PMMA sorbents. The Arg loading in the sorbents was 20 wt.%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Water solubility of Arg before and after complex formation.

Sample	Arg solubility (g/ml)
Arg	0.06
Arg/HTAB (molar ratio ^a of 1:1)	0.07
Arg/S-20 (molar ratio ^a of 1:1)	0.08
Arg/SDS (molar ratio ^a of 1:1)	0.09
Arg/PSS (molar ratio ^a of 2:1)	0.15
Arg/PSS (molar ratio ^a of 1:1)	0.3
Arg/PSS (molar ratio ^a of 1:2)	0.5

^a Molar ratio of Arg to the monomer of corresponding polymer.

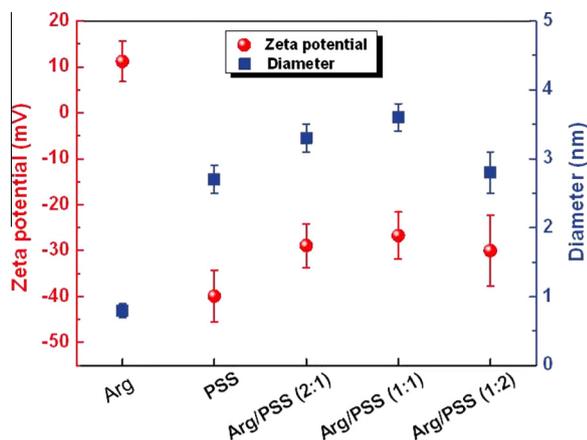


Fig. 5. Zeta potential and size of Arg, PSS, and Arg/PSS complexes. Ratios in parentheses are the molar ratios of Arg to PSS monomer.

had negative charges with zeta potential values of approximately -30 mV (Fig. 5). The complex size of Arg/PSS was about 3 nm (Fig. 5). Upon freeze-drying, particles were formed where the

Arg/PSS complex (1:1 M ratio) formed nanoparticles of ~ 100 nm and, by contrast, pure Arg formed much larger microsized crystals (Fig. 6). These results demonstrated that nano-scale complexes could be formed and large crystal formation could be inhibited by mixing Arg with polymers like PSS.

AA-complexes were subsequently used to develop AA-complex based solid sorbents. PMMA microspheres were mixed with aqueous AA-complex solutions followed by solvent evaporation (Supporting information, Fig. S1). We found that, at the same level of Arg loading, Arg/PSS-PMMA sorbents had substantially higher CO_2 adsorption capacity compared to Arg-PMMA sorbents (Fig. 7). The higher the molar ratio of Arg to PSS monomer, the higher the CO_2 adsorption capacity (Fig. 7); the CO_2 adsorption capacity of Arg/PSS-PMMA sorbents [$0.5 \text{ mol-CO}_2/(\text{kg sorbent})$] at

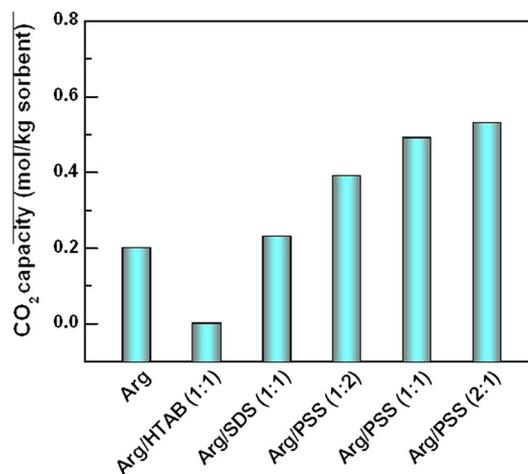


Fig. 7. CO_2 adsorption capacity of Arg and Arg-complex based PMMA sorbents. The ratios in parentheses represent the molar ratio of Arg to the monomer of the corresponding polymer. Arg content in all samples was 10 wt.%.

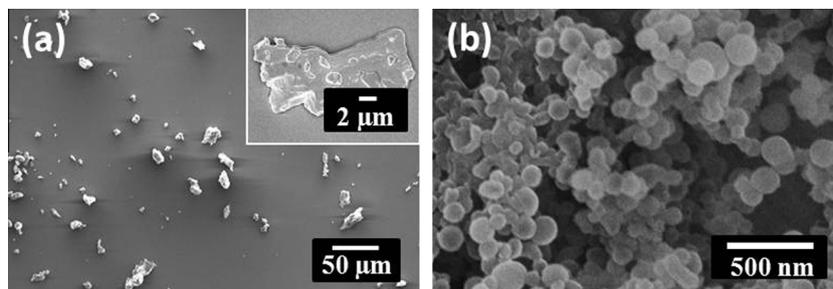


Fig. 6. SEM images of (a) Arg and (b) Arg/PSS complex upon freeze-drying. In (b), the molar ratio of Arg to PSS monomer was 1:1.

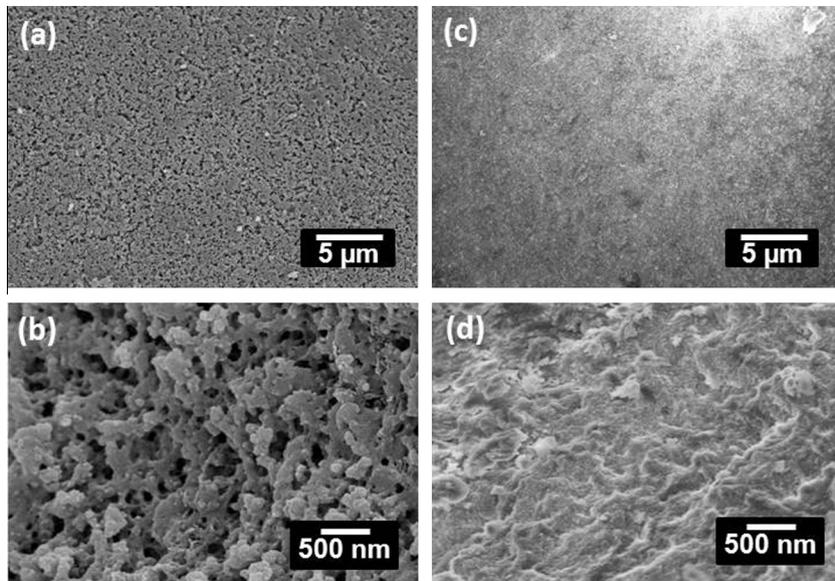


Fig. 8. SEM microstructures of (a and b) Arg/PSS- and (c and d) Arg/SDS-PMMA sorbents. (a and c) Sorbent surface and (b and d) cross-sectional surface inside the sorbents. The molar ratio of Arg to the monomers of PSS and SDS was 1:1.

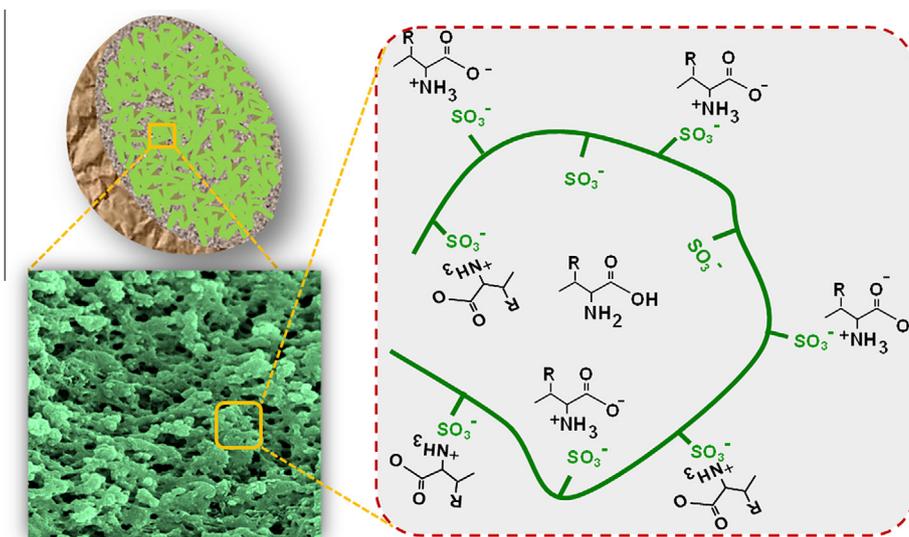


Fig. 9. Schematic illustration of CO_2 interaction with AA-complexes (e.g. Arg/PSS) in solid sorbents.

the Arg/PSS monomer molar ratio of 2:1 was 2.5 times of that of Arg-PMMA sorbents [$0.2 \text{ mol}\cdot\text{CO}_2/(\text{kg sorbent})$]; the Arg loading in both sorbents was 10 wt.% (Fig. 7). Meanwhile, complexing Arg with SDS did not lead to significant enhancement of CO_2 adsorption capacity (Fig. 7). The differences in CO_2 adsorption capacity among Arg/PSS-, Arg/SDS-, and Arg-PMMA sorbents were probably attributed to differences in their sorbent microstructures. One can see that Arg/PSS-PMMA sorbents had porous structures both inside and outside the PMMA microspheres and the distribution of Arg/PSS complexes was uniform inside the microspheres (Fig. 8a and b). By contrast, Arg/SDS-PMMA sorbents had a much denser microstructure both inside and outside (Fig. 8c and d), and as aforementioned, Arg-PMMA had non-uniform Arg distribution and formation of large Arg particles or crystals (Fig. 4). Therefore, Arg/PSS-PMMA sorbents retained highly porous structures which could provide effective channels for the diffusion of CO_2 molecules toward and away from the CO_2 -adsorbing molecules (i.e. Arg). In addition, the interaction between Arg and the strong

polyelectrolyte PSS (Fig. 9) might have weakened the potential hydrogen-bond interactions among Arg molecules [54] thereby inhibiting crystal formation. The primary and secondary amino groups in Arg can react with CO_2 to form carbamates [30]; however, the majority of such groups would be inaccessible upon the formation of large Arg particles or crystals in the case of Arg-PMMA sorbents.

Most importantly, the CO_2 adsorption capacity of Arg/PSS-PMMA sorbents was substantially improved via controlling the loading of Arg/PSS complexes. The CO_2 adsorption capacity of Arg/PSS-PMMA sorbents was found to increase and then decrease with increasing Arg/PSS loading, and a CO_2 adsorption capacity of $1.3 \text{ mol}\cdot\text{CO}_2/(\text{kg sorbent})$ was achieved at 25 wt.% loading (Fig. 10). The CO_2 adsorption capacity of Arg/PSS-PMMA sorbents is comparable to the newly reported propylamine-functionalized mesoporous silica sorbents which had a capacity of $1.4 \text{ mol}\cdot\text{CO}_2/(\text{kg sorbent})$ at 25°C and 1 atm [41]. It is worth noting that the sorption rate and capacity of Arg/PSS-PMMA sorbents in flue gas

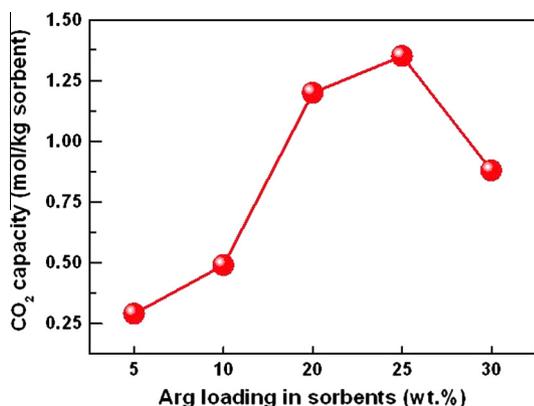


Fig. 10. CO₂ adsorption capacity vs. Arg loading in Arg/PSS-PMMA sorbents.

from power plants are expected to decrease due to lower CO₂ partial pressure [47]. Similar to other amine sorbents, higher loading of Arg/PSS (30 wt.% of Arg) likely blocked the porous channels of the sorbents, causing CO₂ diffusion limitations [1], and leading to reduced CO₂ adsorption capacity. It was generally believed that a CO₂ adsorption capacity of >1.0 mol·CO₂/(kg sorbent) may potentially be practical for industrial CO₂ removal [55].

It is worth noting that AA solvents have recently attracted great interest for CO₂ removal [22–27]. However, AA solvents often require an equimolecular amount of base (e.g. KOH) to free their amino groups which otherwise would be protonated [56,57]. As a result, most AA solvents are highly basic (e.g. pH 11 or higher) leading to equipment corrosion concerns in practical uses. Our developed AA-complex based solid sorbents would eliminate the concerns related to potential equipment corrosion as well as high heat duty associated with aqueous solvent regeneration all the while retaining the advantageous properties of AAs including their high thermal stability, excellent biocompatibility, and negligible volatility. Considering that CO₂ is a massive emission worldwide, long-term stability and low-cost regeneration of AA-complex based solid sorbents are important and will be addressed in future studies. For instance, the regeneration of AA-complex based solid sorbents can be carried out through a temperature-swing process. Loss of sorption capacity may occur during multiple cycles but may be reduced via stabilizing AA-complexes within sorbents through covalent bonding [58,59].

4. Conclusions

This report describes the attempt to immobilize AAs and AA-complexes into porous PMMA microspheres to construct robust solid sorbents for CO₂ removal. Due to its low water solubility, pure AAs formed large particles or crystals inside PMMA microspheres resulting in low CO₂ adsorption capacity. By contrast, immobilization of Arg/PSS complexes into porous PMMA microspheres significantly enhanced the CO₂ adsorption capacity. This is probably because Arg/PSS complex based sorbents had highly porous structures that allowed easy diffusion of CO₂ into and out of the porous support thereby leading to enhanced CO₂ adsorption capacity. SEM imaging confirmed that Arg/PSS-PMMA sorbents had fine microstructures and no large particles or crystals were observed, zeta potential experiments showed that the Arg/PSS complexes were at the nanometer scale, and the developed Arg/PSS complex based sorbents could be innovative for CO₂ removal.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apenergy.2013.03.070>.

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