



## Clover leaf-shaped Al<sub>2</sub>O<sub>3</sub> extrudate as a support for high-capacity and cost-effective CO<sub>2</sub> sorbent

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### ABSTRACT

Amine-functionalized clover leaf-shaped Al<sub>2</sub>O<sub>3</sub> extrudates (CA) were prepared for use as CO<sub>2</sub> sorbent. The as-synthesized materials were characterized by N<sub>2</sub> adsorption, XRD, SEM and elemental analysis followed by testing for CO<sub>2</sub> capture using simulated flue gas containing 15.1% CO<sub>2</sub>. The results showed that a significant enhancement in CO<sub>2</sub> uptake was achieved with the introduction of amines into CA materials. A remarkably high volume-based capacity of 70.1 mg/mL of sorbent of this hybrid material suggests that it can be potentially used for CO<sub>2</sub> capture from flue gases and other stationary sources, especially those with low CO<sub>2</sub> concentration. The novel adsorbent reported here performed well during prolonged cyclic operations of adsorption–desorption of CO<sub>2</sub>.

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### 1. Introduction

Carbon dioxide is presently receiving much attention as one of the main anthropogenic contributors to climate change. A large fraction of CO<sub>2</sub> released into the atmosphere comes predominantly from the combustion of fossil fuels including coal, petroleum and natural gas [1]. Fossil fuels will likely remain our main sources of energy in the 21st century and therefore, it is important to find ways to efficiently and economically capture the CO<sub>2</sub> released from sources such as fossil fuel burning power plants and cement and steel factories. To reduce the CO<sub>2</sub> release from these stationary sources, several research groups have focused on the CO<sub>2</sub> capture by adsorption using sorbents loaded with amines [2–9]. Besides their high capacity and selectivity for CO<sub>2</sub>, these supported amine sorbents have high capacity and selectivity for CO<sub>2</sub> and are tolerant to water vapor. They could operate near ambient conditions and can be regenerated by mild temperature swing or concentration swing processes. Therefore, these materials are considered as one of the most promising sorbents for CO<sub>2</sub> capture. However, the support materials currently used in the preparation of the supported amine sorbents are mainly the mesoporous silica materials such as MCM-41 [10], SBA-15 [11,12], SBA-16 [13], KIT-6 [14] and MCF [15]. These materials are presently not commercially available in large quantities and they may not be cost-effective as the cost for their

preparation can be very high. It was estimated that the cost of the support materials accounts for more than 90% of the total cost of the supported amine adsorbents [16]. Therefore, it is obvious that reducing the cost of the support can significantly reduce the cost of the adsorbent.

To reduce the cost of amine supported sorbents, several cost-effective materials were explored as the support for CO<sub>2</sub> capture through amine modification. These include commercially available carbon-based materials [16] and fumed silica [17]. Mesoporous silicas synthesized by using rice husk ash as silica source were also proposed [18]. However, the above adsorbents are powder materials and therefore, their volume adsorption capacity is relatively low because of interparticle porosity. In addition, they are difficult to use in practice because of the high pressure drop over the sorbent and dust pollution. Therefore, it is necessary to develop a new adsorbent with the ideal characteristics of high CO<sub>2</sub> sorption capacity, low cost and low pressure drop. Here we report on the design and synthesis of a potentially ideal alumina-based and amine-loaded sorbent for CO<sub>2</sub> capture.

Commercial aluminas usually exhibit high surface area, large total pore volume and broad pore size distribution. In addition, the forming or shaping of alumina materials is very easy to accomplish. Therefore, shaped alumina can be an ideal support for potential CO<sub>2</sub> capture after amine impregnation. In this work, a series of amine-functionalized clover leaf-shaped Al<sub>2</sub>O<sub>3</sub> extrudates were prepared by a simple impregnation method. The as-synthesized sorbents were characterized by N<sub>2</sub> adsorption, XRD, SEM, and elemental analysis. The effect of amine content on the performance of the

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adsorbents for CO<sub>2</sub> capture was investigated. Moreover, the regeneration stability of the selected adsorbent was also conducted with several cycles of adsorption–desorption of CO<sub>2</sub>.

## 2. Experimental

### 2.1. Preparation of amine-modified clover leaf-shaped Al<sub>2</sub>O<sub>3</sub> extrudates

The clover leaf-shaped Al<sub>2</sub>O<sub>3</sub> extrudates (denoted hereinafter as CA) were prepared in the laboratory with an external diameter of 1.3 mm and an average length of 4 mm. Briefly, the procedure to prepare clover leaf-shaped alumina is as follows: pseudo-boehmite was mixed with an aqueous solution containing 20 wt% nitric acid to form homogeneous dough, which was then extruded using a clover leaf-shaped extruder. After extrudation, the formed materials were dried at 110 °C overnight and calcined at 550 °C for 3 h to convert the boehmite to  $\gamma$ -alumina. The polyethyleneimine (PEI) impregnated clover leaf-shaped Al<sub>2</sub>O<sub>3</sub> extrudates were prepared according to a procedure reported in [19]. Specifically, a given amount of PEI (Aldrich, average molecular weight 423, linear type, b.p. 250 °C) was dissolved in 15.0 g of methanol under stirring for 30 min, and then 2 g of clover leaf-shaped alumina was added to the mixture. The resultant mixture was continuously stirred for about 8 h and then dried at 70 °C over night. The obtained sorbents were denoted as CA/x, where x represents the weight percentage of PEI in the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>).

### 2.2. Characterization

Powder XRD patterns were obtained using a Panalytical Xpert PRO X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm, 40 kV, 40 mA). The N<sub>2</sub> adsorption–desorption isotherms were collected at 77 K using Micromeritics TriStar 3000 Porosimeter. The adsorbent was degassed prior to each measurement at 100 °C in a high vacuum for 3 h. The surface area ( $S_{\text{BET}}$ ) was calculated using the BET method. The total pore volume ( $V_t$ ) was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99 and the pore size ( $D$ ) was calculated from the desorption isotherm using the BJH method. The amounts of nitrogen introduced to the CA samples were measured with the help of a Vario EL III elemental analyzer. The morphological features were observed in a scanning electron microscope (SEM) (Hitachi S-4800) by examining the cross section of the samples. The tap density of each sorbent was determined by measuring the volume of a known weight of the sorbent after continuously tapping for 2 min. Each experiment was performed 3 times i.e., triplicates were used.

### 2.3. CO<sub>2</sub> capture

The CO<sub>2</sub> capture by the adsorbent in simulated flue gas was measured with a packed bed flow reactor as described previously [11]. 1.5 g of a dried adsorbent was loaded into the bed. Prior to each adsorption measurement, the sorbent was treated by heating at 100 °C for 1 h in Ar stream at a flow rate of 15 ml/min. After cooling to the desired temperature, an N<sub>2</sub> stream containing 15.1 v/v% CO<sub>2</sub> at a total flow rate of 10 ml/min was introduced and passed through the sorbent. The CO<sub>2</sub> concentrations in the effluent gas streams were measured with an online gas chromatograph. Blank experiments were also conducted to eliminate the overestimation of CO<sub>2</sub> uptake caused by mass transfer limitation. An inert gas (He) was introduced to see how long it took for the breakthrough to occur. The CO<sub>2</sub> uptake of the adsorbent was calculated by integrating the area between the inert gas and CO<sub>2</sub> breakthrough curves.

In the CO<sub>2</sub> adsorption/desorption cycle experiment, each sample was firstly heated at 100 °C for 1 h in Ar, then cooled down to

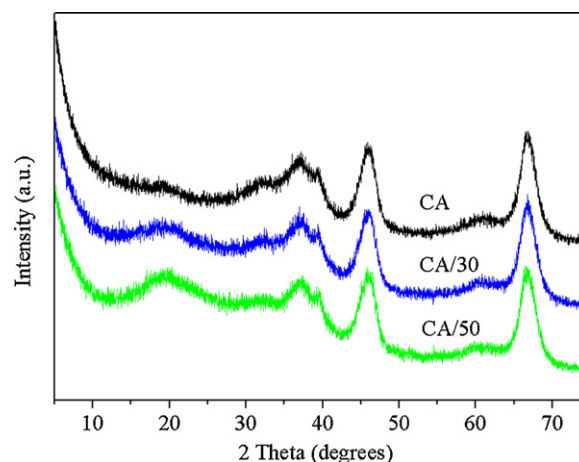


Fig. 1. XRD patterns of CA, CA/30 and CA/50 samples.

75 °C prior to exposure to the 15.1 v/v% CO<sub>2</sub> (N<sub>2</sub> as balance gas) flow (10 mL/min) for 100 min. After that, the sorbent was kept at the same temperature in Ar flow (15 mL/min) for 150 min for sorbent regeneration. The same sorption–desorption procedure was conducted for 8 cycles to test for cyclic stability of the sorbent.

## 3. Results and discussion

### 3.1. Characterization

Fig. 1 shows the XRD patterns of the representative samples of CA treated with 0%, 30% and 50% PEI amounts. All the samples exhibited distinct peaks at 38.6°, 44.6°, and 66.7°, respectively, which can be attributed to the well-crystallized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and match with the standard pattern. Interestingly, both CA/30 and CA/50 samples show a very diffuse reflection near  $2\theta = 20^\circ$ , which could be attributed to the correlation distance between aggregated PEI molecules inside the framework pores as suggested previously [20]. Moreover, with the increase of the PEI content, the intensity of the above diffraction peak increased. When the loading amount of PEI increased in CA materials, both the specific surface area and pore volume decreased but the tap density increased (Table 1). For instance, the CA/20 sample with amine loadings of 4.82 wt% N/g had a BET surface area of 121 m<sup>2</sup>/g, a pore volume of 0.39 cm<sup>3</sup>/g and a tap density of 0.62 mL/g, whereas those of the unmodified CA used in this experiment correspond to 235 m<sup>2</sup>/g, 0.66 cm<sup>3</sup>/g and 0.47 mL/g, respectively (Table 1). The CA adsorbents with higher amine loadings, such as CA/60, showed a more significant decrease in surface area and pore volume but an increase in tap density. Both the surface area and pore volume decreased with increased PEI loading because the PEI molecules were mostly loaded inside the pores [21]. This observation of surface area and pore volume is consistent with the XRD characterization, which suggested that most of the PEI occupied the pore space of the CA (vide supra). Fig. 2 shows the clover leaf-shaped CA extrudate (control) and the cross-sectional SEM images of CA samples treated with 0%, 40% and 60% PEI. The CA/40 sample treated with 40% of the amine still retained the original morphology of CA (compare Fig. 2b with 0% PEI to Fig. 2c with 40% PEI treatment). However, when the amine loading amount increased to 60%, all the pores were almost filled by PEI and a smooth surface resulted with the CA/60 sample (Fig. 2d). Elemental analysis revealed that the PEI content of the resulting sorbents was lower than the initial amount of PEI added during the preparation process (Table 1). This result indicated that a relatively large amount of PEI remained in the container during the impregnation process. The excess PEI was found to stick to the inside of

**Table 1**  
Textural properties and CO<sub>2</sub> uptake of PEI-modified CA samples.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>t</sub> (cm <sup>3</sup> /g)	D (nm)	Tap density (mL/g)	N (wt%)	PEI <sup>a</sup> (wt%)	CO <sub>2</sub> uptake (mg/g)	CO <sub>2</sub> uptake (mg/mL)
CA	235	0.66	7.2	0.47	0	0	23.2 <sup>b</sup>	49.3 <sup>b</sup>
CA/20	121	0.39	6.5	0.62	4.82	14.8	26.7	43.0
CA/30	75	0.28	6.7	0.71	6.58	20.2	49.8	70.1
CA/40	65	0.25	7.3	0.75	7.71	23.7	45.5	60.6
CA/50	34	0.16	8.4	0.79	9.3	28.6	49.0	62.0
CA/60	11	0.08	9.5	0.84	10.86	33.4	17.4	20.7

<sup>a</sup> Values were calculated according to elemental analysis.

<sup>b</sup> CO<sub>2</sub> capture was performed at 25 °C.

the container and therefore, it could be reused for the subsequent preparation of amine-modified sorbents.

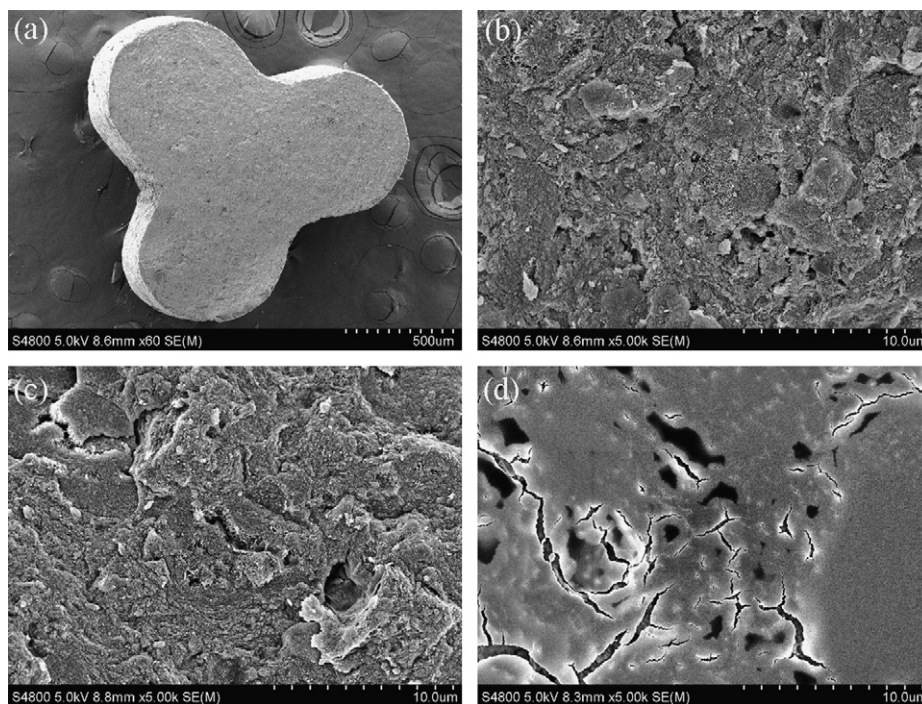
### 3.2. CO<sub>2</sub> capture

Previous studies showed that PEI impregnated mesoporous materials showed the optimum CO<sub>2</sub> adsorption performance at 75 °C because this higher temperature facilitated the transfer of the adsorbed CO<sub>2</sub> molecules from the surface into the bulk of PEI encapsulated in the porous substrate [6,11]. Therefore, the CO<sub>2</sub> sorption test was conducted at 75 °C in this study for the amine impregnated samples. For pure CA sample, the adsorption process was performed at 25 °C (Table 1) because low temperature facilitates the CO<sub>2</sub> adsorption as the adsorption of CO<sub>2</sub> into CA is a thermodynamically controlled process. Fig. 3 shows the influence of PEI loading amount in CA on CO<sub>2</sub> adsorption from N<sub>2</sub> containing 15.1 v/v% CO<sub>2</sub> at atmospheric pressure. Breakthrough times of CO<sub>2</sub> were in the following order: CA < CA/20 < CA/30 (Fig. 3A). The steep slope observed for all three samples tested indicates that the CO<sub>2</sub> diffusion from the surface into the bulk of materials occurred very quickly i.e., with easy mass transfer and very fast kinetics. When the PEI content increased from 23.7 wt% (CA/40) to 28.6 wt% (CA/50), the adsorption rate decreased as can be seen from Fig. 3B. However, with further increase of the PEI content to 33.4 wt% (CA/60), the adsorption rate increased. This result indicated that with large amount of PEI (>23.7 wt%) impregnation, the

blockage of pores was severe and therefore, the CO<sub>2</sub> could hardly diffuse through the surface to the centre of adsorbent, leading to a lower CO<sub>2</sub> adsorption rate. However, with further increase of the PEI content to 33.4 wt%, because a large proportion of the pores in the adsorbent were blocked, the CO<sub>2</sub> could not diffuse into the bulk of materials. Therefore, the amount of CO<sub>2</sub> uptake of CA/60 sample decreased significantly (Table 1), whereas the adsorption rate increased. Among the PEI modified CA samples, CA/30 showed high CO<sub>2</sub> adsorption rate and the highest CO<sub>2</sub> uptake of 49.8 mg/g of sorbent (70.1 mg/mL of sorbent) (Table 1). Compared with the previously reported best CO<sub>2</sub> sorbent prepared from PEI loaded carbon materials [16], CO<sub>2</sub> uptake capacity by weight of CA/30 is lower, but the volume-based capacity is higher by a factor of 1.5. This is one of the highest capturing capacities reported to date in the literature on a volume basis under the given conditions. In addition, the estimated cost for CA/30 sorbent is less than \$30/kg, which is lower than that of low-cost carbon-based sorbent (~\$44/kg) and much lower than that of SBA-15-based sorbent (~\$760/kg) [16].

### 3.3. Adsorbent regenerability

Regenerability of the adsorbents is another important issue for practical application. Therefore, multiple cycles of adsorption–desorption tests were performed on CA/30 sample at 75 °C. As shown in Fig. 4, a slight decrease in the CO<sub>2</sub> uptake was observed with increasing number of sorption/desorption



**Fig. 2.** The cross-sectional SEM images of (a) CA, (b) CA, (c) CA/40 and (d) CA/60 samples.

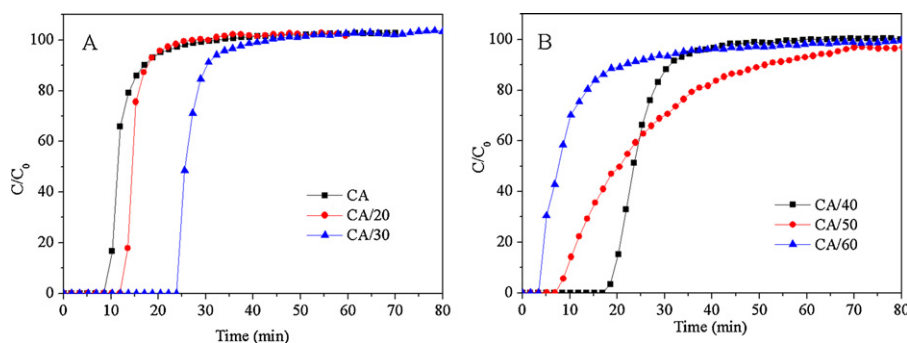


Fig. 3. CO<sub>2</sub> breakthrough curves of CA with different loading amounts of PEI.

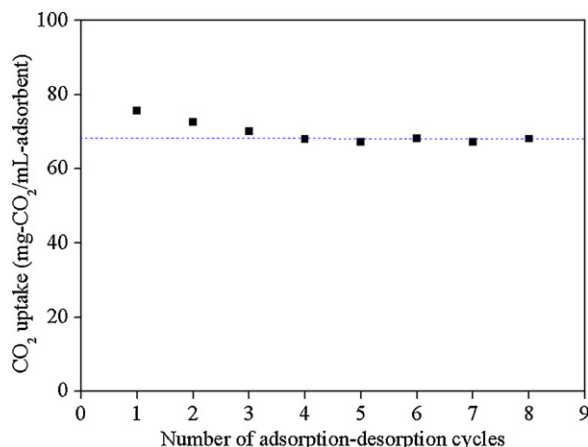


Fig. 4. CO<sub>2</sub> adsorption-desorption cycles on CA/30 sample at 75 °C.

cycles. However, such a drop became insignificant with increasing number of cycles as indicated by the flat curve (Fig. 4). The present results showed that about 90% of the initial CO<sub>2</sub> uptake could be retained after 8 cycles.

#### 4. Conclusions

Clover leaf-shaped Al<sub>2</sub>O<sub>3</sub> extrudates were found to be excellent supports for the immobilization of PEI and these may serve as cost-effective sorbents for CO<sub>2</sub> capture. A CA sample with 20.2 wt% PEI loading exhibited a high CO<sub>2</sub> uptake of 70.1 mg/mL of sorbent and also performed well with repetitive adsorption-desorption cycles.

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