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Fly Ash-derived Solid Amine Sorbents for CO₂ Capture from Flue Gas

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Abstract

CO₂ capture and storage from flue gas has been considered as a key option for greenhouse gas control. The challenge of CO₂ capture is the high energy penalty resulting into the high capture cost. In this paper, it is reported that solid amine sorbents can be synthesized from fly ash successfully and they can be applied for CO₂ capture from flue gas. The sorbent, PEI/FA, has improved sorption performance and allowed a low production cost. The effects of sorption temperature and PEI loading amount on CO₂ sorption capacity were investigated. The CO₂ sorption capacity, CO₂ sorption rate and the regenerability of PEI/FA were evaluated by using thermogravimetric analyser (TGA). The highest CO₂ sorption capacity of PEI/FA sorbents is 145.0 mg-CO₂/g-sorbent at 90 °C under 10 % CO₂ in N₂. Comparing with the sorbents, which have the similar sorption capacity, the preparation cost of PEI/FA is significantly reduced. The multi-cycles of PEI/FA were conducted and the sorption capacity of the regenerated sorbent after 100 cycles was still maintain 90% of the initial sorption capacity. The sorbent also shows a fast CO₂ sorption rate and the CO₂ sorption capacity can reach about 75 % of saturation capacity at first 2 min. The results indicate that the PEI/FA synthesized by this environmental friendly and low cost method has potential application for low temperature CO₂ capture in terms of its outstanding features such as high capture capacity, fast sorption/desorption rate, good regenerability, no corrosion and cost-effective.

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Keywords: CO₂ sorbent; CO₂ capture; fly ash; sol-gel impregnation method

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1. Introduction

It is widely accepted that the amount of CO₂ has risen in the atmosphere from fossil fuels burning, which contributes to climate change [1-5]. CO₂ capture and separation from flue gases have been considered as a key opportunity to reduce the greenhouse gases emissions from the power plant in the short term [6-8]. Meanwhile, large amount of fly ash (FA) is produced by coal fired power plant, which is piled up cause to environmental pollution and cultivated land wasting [9, 10]. Ideally, conversion of fly ash into the products that can capture CO₂ has been actively pursued to achieve economic gains and environment protection [11].

Recently, several researchers have made progress in the synthesis of fly ash derived solid amine sorbents. The synthesis methods can be classified into two major types: one is the directly surface modification fly ash, another is the modified porous materials derived from fly ash carbon sorbents, and the CO₂ sorption capacity of the best sample was 7.7 mg-CO₂/g-sorbent. For the other type, Arenillas’s [13] group and Maroto-Valer’s [14] group used carbon materials from fly ash as the support to load amine, and the sorption capacity of the sorbents was 45 mg-CO₂/g-sorbent and 68.6 mg-CO₂/g-sorbent, respectively. Chen’s [15] group prepared the mesoporous alumina (MA) derived from fly ash, and sorbents achieved CO₂ sorption capacity 120 mg-CO₂/g-sorbent after loading PEI on MA. Chandrasekar’s [16] group used the silicate species from fly ash to prepare the SBA-15, and then obtained the CO₂ sorption sorbents after PEI loading into the SBA-15. The best sample PEI-FSBA-15 gave a sorption capacity of 110 mg-CO₂/g-sorbent. Franchi’s [17] group used the MCM-41 from fly ash as the support of the solid amine sorbents and the sorption capacity is 103.8 mg-CO₂/g-sorbent. However, the synthesis process of the molecular sieve as the support material is complex and expensive. It limits the practical application of these sorbents in the large-scale CO₂ capture form flue gas [18, 19]. Therefore, the development of a straightforward method which can obtain a good CO₂ sorption performance sorbent is desirable.

In this work, a novel synthesis method is reported for a solid amine sorbents preparing from fly ash. This method can allow more PEI loading than the traditional wet impregnation (WI) method dose. Moreover, the sorbent has great advantages including simple preparation process, good CO₂ sorption performance and cost-efficiency.

2. Experimental

2.1. Preparation of solid amine sorbent from fly ash

The PEI/FA samples: a supernatant solution of silicate species extracted from fly ash by alkali fusion was used to prepare the silica support. The weight ratio of the reaction mixture was 1 fly ash: 0.5 NaOH: 2 H₂O stirring at 90 ℃ for 1 h. After filtration, the extracted supernatant solution was obtained which contained massive silicate. Carbon dioxide was blown into the extracted supernatant solution which was stirring at desired temperature until the pH value dropped to 10, and the wet silica gel was produced after filtering. The powder was formed from wet gel after drying. The powder was named as the white carbon black (WCB). A certain amount of PEI was dissolved in the ethanol, and then desired amount of wet silica gel was added to the PEI/ethanol solution. The slurry was continuously stirred at 70 ℃ for about 4–5 h, until the ethanol in the slurry was evaporated. After ethanol was mainly evaporated, the samples were further dried in a vacuum oven at 40 ℃ overnight, and then sealed in sample bags before use. Due to the support is wet gel, we call this novel preparation method as the wet support impregnation method. More details about this method can be found in our previous work [18].

The PEI/FA samples were prepared by a WI method. In a typical preparation, about 1.0 g of PEI was dissolved in 20 ml of ethanol under stirring for ~60 min to make a PEI/ethanol solution, and then desired amount of the WCB from fly ash was added into the PEI/ethanol solution. The slurry was continuously stirred at room temperature for about 5 h, allowing the ethanol in the slurry to be evaporated. After ethanol was mainly evaporated, the sample was sealed in a bottle before test after dried in a vacuum oven.
2.2. Characterization

N₂ adsorption isotherms were measured in an ASAP-2020 instrument at 77 k. The surface area of fly ash and samples were calculated by BET method. The scanning electron microscopy (SEM) images were obtained on a Sirion 200 scanning electron microscope operating at 5 kv. Fourier transform infrared (FTIR) spectra were collected on a VERTEX 70 spectrometer at room temperature.

2.3. CO₂ sorption/desorption performance measurement

The CO₂ sorption/desorption performance of the sorbents was evaluated by using TGA (NETZSCH). A typical analysis is described as below: About 50 mg of the sorbent was placed at the TGA sample pan. The sample was first heated from room temperature to 100 °C at a rate of 10 °C/min under a pure N₂ flow with a flow rate of 80 ml/min. The temperature was kept at 100 °C for 60 min to remove the remained solvent, the sorbed CO₂ and moisture from the sample. The sample was cooled down to the desired sorption temperature and kept at this temperature for 30 min. The sorption was stated by switching the flow as from pure N₂ to 10 v% CO₂ in N₂ at the same flow rate and hold at the sorption temperature for 30 min for CO₂ sorption. After the sorption, the flow gas was switched back to the pore N₂ and the temperature was increased to 100 °C for desorption. The sorption capacity of the sample was calculated according to the mass change during sorption.

3. Results and discussion

3.1. Characterization of the materials and sorbents

The textural properties of the fly ash, WCB derived from fly ash and PEI/FA were calculated by BET method and the results were shown in Table 1. It is clearly shown that the surface area and pore volume of raw fly ash is too limited to load PEI as the support material for CO₂ sorbents. The surface area of WCB from FA is much larger than FA, and it is a kind of potential support for solid amine sorbents.

Moreover, after loading PEI by using WSI method, the surface area and pore volume of PEI/FA was decreased sharply, it indicated that the PEI was filled into the pore channel of the support material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area( m²/g)</th>
<th>Pore volume(cm³/g)</th>
<th>Pore diameter(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash-1</td>
<td>4.99</td>
<td>0.014</td>
<td>3.81</td>
</tr>
<tr>
<td>Fly ash-2</td>
<td>3.12</td>
<td>0.01</td>
<td>3.83</td>
</tr>
<tr>
<td>Fly ash-3</td>
<td>4.68</td>
<td>0.017</td>
<td>3.44</td>
</tr>
<tr>
<td>Fly ash-4</td>
<td>2.74</td>
<td>0.009</td>
<td>3.07</td>
</tr>
<tr>
<td>Fly ash-5</td>
<td>2.12</td>
<td>0.006</td>
<td>3.82</td>
</tr>
<tr>
<td>WCB from FA-1</td>
<td>85.06</td>
<td>0.21</td>
<td>10.85</td>
</tr>
<tr>
<td>PEI/FA</td>
<td>6.36</td>
<td>0.01</td>
<td>8.32</td>
</tr>
</tbody>
</table>

The SEM images of FA and sorbents were shown in Figure 1. Raw fly ash shows different size spheres with smooth surface. The WCB looks like small particles aggregation, which gives larger surface area and pore volume. It could be a kind of support material of solid amine sorbents. PEI/FA look like more viscous than WCB, since the surface and pores of WCB are filled full of amine.
Figure 2 shows the transmission infrared spectra of the PEI, the support (WCB) and the solid amine sorbent at room temperature. The band at 1644 cm\(^{-1}\) can be assigned to hydrogen bonding in molecular H\(_2\)O. After PEI loading, this band decreased significantly. There are new signals appeared after loading PEI on the support. The doublets at 2960 and 2837 cm\(^{-1}\) can be assigned to the C-H of PEI. The bands at 1477 and 1577 cm\(^{-1}\) can be attributed to the deformation of the primary amine groups (-NH\(_2\)). These indicate that the loading PEI stays intact after loading onto the surface of the support.

![Fig. 1. SEM images of (a) fly ash, (b) White carbon black, (c) PEI/FA](image)

![Fig. 2. Transmission infrared spectra of WCB, PEI and the sorbent](image)
3.2. Sorption performance of solid amine sorbent

For application, high CO$_2$ sorption capacity, fast sorption/desorption rate, good regenerability and a wide range of operating conditions would be defined as an ideal sorbent [20]. In this work, several import parameters including CO$_2$ sorption capacity, sorption/desorption rate and regenerability were investigated.

The effect of PEI loading amount on the CO$_2$ sorption capacity was examined by using TGA at 75 °C under flow gas of 10 v% CO$_2$ in N$_2$. As were shown in Figure 3, the WCB alone gave a CO$_2$ adsorption capacity of 5.6 mg-CO$_2$/g-sorbent, indicating that the reaction between CO$_2$ and WCB was a weak physic adsorption. The CO$_2$ sorption capacity of PEI/FA both from WSI and WI increased to a maximum point and then decreased with PEI loading amount increasing. This is because PEI contains a great number of the potential CO$_2$-philic sites and the support makes these sites accessible through improving the dispersion of PEI. However, when the PEI loading keeps increasing after the maximum point, the excessive PEI is coated on the external surface of the WCB particles, resulting in the agglomeration of the particles. Thus the number of the accessible sorption sites is reduced.

![Fig. 3. Effect of PEI loading amount on sorption capacity](image)

The effect of the sorption temperature on the sorption capacity of PEI/FA was examined using TGA with flow gas of 10 v% CO$_2$ in N$_2$ at 30, 50, 60, 70, 75, 80, 90, 100 and 110 °C, respectively. The results are showed in Figure 4. At 30 °C, the CO$_2$ sorption capacity of PEI/FA was 77.6 mg-CO$_2$/g-sorbent. With temperature increasing, the CO$_2$ sorption capacity became higher and reached the highest capacity of 145.1 mg-CO$_2$/g-sorbent at 90 °C. Continuous increasing temperature from 90 to 110 °C, the sorption capacity decreased to 95.8 mg-CO$_2$/g-sorbent. The results indicate that at the temperature range from 30 °C to 90 °C, the diffusion of CO$_2$ in the PEI may be a kinetic control step. Consequently, elevating temperature results in the increase of the number of accessible amine sites in the sorbent, and thus increases the CO$_2$ sorption capacity. When the temperature is higher than 90 °C, the thermodynamics may play a dominant role, thus resulting in the decrease of the sorption capacity with increasing temperature.
Regenerability of the sorbents is extremely important from a practical perspective. In the present study, desorption was performed by switching the flue gas to pure N₂ gas. The 100 sorption/desorption cycles of PEI/FA were conducted by using TGA. The sorption was at 75 °C and the desorption was at 100 °C. The measured sorption capacities as a function of the cycle number are shown in Figure 5. The sorption capacity decreased slightly with increasing cycle number was observed. The sorption capacity of the regenerated sorbent after 100 cycles was still maintain 85% of the initial sorption capacity. The sorbents shows a good regenerability during multi-cycles. The gradual degradation of the CO₂ sorbents may be due to the formation of urea groups. Further investigation is necessary to clarify the reason.
4. Conclusions

A wet-support impregnation synthesis method was successfully developed for preparing the CO₂ capture sorbents. This method has two obvious advantages, one is to improve the PEI loading percentage and the other is to induce uniform dispersion of PEI in the support. The best sorbent gave a high sorption capacity 145.0 mg-CO₂/g-sorbent prepared by wet-gel impregnation method, which increased by ~80% that prepared by WI method. This kind of sorbents also showed a good regenerability, since it could keep 85% initial capacity after 100 sorption/ desorption cycles. The result indicates that the fly ash-based solid amine sorbent is promising for large-scale CO₂ capture from flue gas due to its high sorption capacity, and low preparation cost. However, there are still a lot of challenges for the practical application of this sorbent for CO₂ capture from flue gas, including the stability, regeneration method and the mass and heat transfers in the scale up of the process.

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References