Enhanced CO$_2$ adsorptive performance of PEI/SBA-15 adsorbent using phosphate ester based surfactants as additives

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ABSTRACT

In this study, a series of polyetherimide/SBA-15: 2-D hexagonal P6mm, Santa Barbara USA (PEI/SBA-15) adsorbents modified by phosphoric ester based surfactants (including tri(2-ethylhexyl) phosphate (TEP), bis(2-ethylhexyl) phosphate (BEP) and trimethyl phosphonoacetate (TMPA)) were prepared for CO$_2$ adsorption. Experimental results indicated that the addition of TEP and BEP had positive effects on CO$_2$ adsorption capacity over PEI/SBA-15. In particular, the CO$_2$ adsorption amount could be improved by around 20% for 45PEI–5TEP/SBA-15 compared to the additive-free adsorbent. This could be attributed to the decrease of CO$_2$ diffusion resistance in the PEI bulk network due to the interactions between TEP and loaded PEI molecules, which was further confirmed by adsorption kinetics results. In addition, it was also found that the cyclic performance of the TEP-modified adsorbent was better than the surfactant-free one. This could be due to two main reasons, based on the results of in situ DRIFT and TG-DSC tests. First and more importantly, adsorbed CO$_2$ species could be desorbed more rapidly over TEP-modified adsorbent during the thermal desorption process. Furthermore, the enhanced thermal stability after TEP addition ensured lower degradation of amine groups during adsorption/desorption cycles.

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Introduction

As the climate change problem becomes more and more severe, much attention is being paid to technologies for CO$_2$ capture, the major greenhouse gas (GHG). Due to some intractable problems faced by fluid absorption technologies involving monoethanolamine (MEA) solutions, such as corrosion of equipment and difficulties with regeneration, solid adsorption technology has been considered as a prospective alternative. A great deal of work has been done to develop high-performance absorbents for CO$_2$ capture in the last three decades, such as zeolites (Franchi et al., 2005; Harlick and Tezel, 2004; Inui et al., 1988; Barrer and Gibbons, 1964; Siriwardane et al., 2003; Walton et al., 2006; Zukal et al., 2010), metal-organic frameworks (MOFs) (Bourrelly et al., 2005; Caskey et al., 2008; Férey, 2008; Llewellyn et al., 2006; Millward and Yaghi, 2005; Yaghi et al., 2003), carbon nanotubes (CNTs) (Cinke et al., 2003; Huang et al., 2007; Su et al., 2009), and pillared lamellar clays (Ram Reddy et al., 2006). Among them, the polymeric amine-containing hybrid adsorbents (Tsuda and Fujiwara, 1992; Walton et al., 2006; Xu et al., 2002) have been investigated extensively in recent years due to their advantages such as high CO$_2$ capacity (Ma et al., 2009; Qi et al., 2011), high selectivity of CO$_2$ over N$_2$ (Belmabkhout et al., 2010) and appropriate adsorption/desorption temperatures (Harlick and Sayari, 2006; Xu et al., 2003).

For supported-amine materials, the CO$_2$ adsorption capacity has been found to be strongly affected by the amount of...
amines loaded. Increasing the loading content of amines enhances the adsorption capacity for CO₂. However, as the amount of loaded-amine approaches an upper limit according to the pore volume of the supports, strong diffusion limitations for CO₂ molecules from the surface into the bulk of the loaded amines, due to their agglomeration, tends to lower the amine efficiency to some extent (Xu et al., 2003; Zhang et al., 2013). Furthermore, many previous studies (Chen et al., 2009, 2013; Franchi et al., 2005; Harlick and Sayari, 2006; Ma et al., 2009; Son et al., 2008; Wang et al., 2013) confirmed that CO₂ adsorption in the supported-amine materials is a diffusion-limited process. As such, many efforts have been made to improve CO₂ diffusion performance over amines supported on mesoporous materials.

Yue et al. utilized as-prepared SBA-15 (Yue et al., 2006) and MCM-41 (Yue et al., 2008) (without removing the templates) as the amine supporter for CO₂ adsorption. It was found that the loaded amine (TEPA, tetraethylpentamine) molecules dispersed in the channels of mesoporous silica were highly accessible to CO₂ molecules, as the preserved template could inhibit amine aggregation, thereby enhancing the CO₂ adsorptive capacity. Fauth et al. (2012) and Heydari-Gorji et al. (2011) concluded that surface 3-aminopropyl and alkyl chains could spatially disperse the subsequently loaded amine molecules, facilitating CO₂ adsorption/desorption kinetics in the inner PEI (polyethyleneimine) network. Similar findings have been reported in our previous study (Liu et al., 2013a), that the introduction of CO₂-neutral surfactants as additives could break up the compact PEI molecules and create extra CO₂ transfer pathways, boosting CO₂ diffusion deeper into the PEI films. As such, a dramatic enhancement in CO₂ capacity was obtained.

However, many of studies had also indicated that better dispersion of amine polymer into smaller size particles with higher volatility in nanoporous supports would lead to the decomposition of the polymers at lower temperatures (Liu et al., 2013b; Son et al., 2008; Xu et al., 2003). Therefore, both the dispersion and thermal stability of the loaded amine should be guaranteed for the purposes of practical application. Based on these concerns, two phosphate esters (tri(2-ethylhexyl) phosphate (TEP) and bis(2-ethylhexyl) phosphate (BEP)) were employed in this work as surfactant and stabilizer for the PEI/SBA-15 adsorbents, as they possessed properties such as good thermal stability and surface dispersion ability (Lü and Chen, 2005). Then, their CO₂ adsorptive performances (including adsorption capacity, cyclic performance, and kinetics) were investigated. Another phosphorus ester (trimethyl phosphonoacetate (TMPA)) was used for comparison.

1. Materials and methods

1.1. Sample preparation

SBA-15 was purchased from Nanjing (JCNANO Tech Co., LTD., Nanjing, Jiangsu, China). Details of its textural properties are provided in supporting information. All other chemicals used were purchased (Aladdin Chemistry Co., LTD., Shanghai, China) and were used without further treatment.

Three phosphorus-containing surfactants, including tri(2-ethylhexyl) phosphate (TEP), bis(2-ethylhexyl) phosphate (BEP), and trimethyl phosphonoacetate (TMPA), were employed as additives to investigate their effects on the CO₂ adsorption performance of the adsorbents. The adsorbents were prepared by a wet impregnation method. In a typical preparation, the desired amounts of PEI (M₅₆ = 600) and additive were dissolved in 40 mL of methanol at room temperature with continuous stirring for 30 min, and then 2.0 g of the mesoporous silica SBA-15 was added to the above solution and further stirred for 2.5 hr, followed by a drying step in vacuum at 80°C to obtain the adsorbent. The resulting adsorbents were denoted as αPEI-β/surfactant/SBA-15, where α refers to the weight percentage of PEI and β to the weight percentage of the surfactants.

1.2. Characterizations

The adsorption–desorption isotherms of nitrogen were obtained at 77 K using the surface area and porosity measurement system (JW-BK132F, Beijing JWGB Sci. & Tech. Co., Ltd, Beijing, China). The specific surface areas of the samples were calculated by the multiple-point Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.3. The total pore volumes, Vₜot, were calculated at P/P₀ = 0.99.

The thermal stability of the investigated samples was tested using thermogravimetry – differential scanning calorimetry (TG/DSC, STA 409 Luxx, Selb, Netzsch, Germany) by heating samples (about 10 mg) from room temperature to 800°C at a heating rate of 10°C/min in an air atmosphere. Elemental analysis was performed on a Flash instrument (EA1112, Thermo Finnigan, Silicon Valley, California, USA). In situ FT-IR was conducted using an in situ DRIFT cell equipped with a gas flow system. The DRIFT measurements were performed with ZnSe windows coupled to a FT-IR spectrometer (Tensor 27, Bruker, Ettlingen, Germany). In the DRIFT cell, samples were pretreated at 105°C in a He environment for 1 hr, followed by CO₂ adsorption at 75°C for 30 min and desorption in pure He at 105°C. The absorption spectrum was obtained by using the formula Aₐₜₐ = lg(1/I₀) – lg(1/I₁), where the background spectrum was recorded in flowing He.

1.3. CO₂ adsorption performance measurements

As described in our previous study (Liu et al., 2013a, 2012), the experimental tests of CO₂ kinetic equilibrium adsorption capacity were carried under atmospheric pressure in a quartz fixed-bed reactor in a furnace equipped with programmable temperature controller. A total of 0.5 g of adsorbent particles in 40–60 mesh was preheated at 105°C for 1 hr in pure N₂ atmosphere, followed by exposure to a 9.5 vol.% CO₂/N₂ mixture until pseudo-equilibrium was reached at 75°C. The outlet CO₂ concentration was recorded by a CO₂ analyzer (G100, Geotech, Warwickshire Leamington Spa, UK). The CO₂ adsorption amount was calculated by integrating the breakthrough curve (shown in Supplementary data) and the detailed calculating formula was provided in our previous work (Liu et al., 2013a). Next, flow was switched to N₂ and the temperature was raised to 105°C and held for another 1 hr. The above-mentioned procedures were repeated 20 times to...
evaluate the extended cyclic adsorption/desorption performance of the samples.

CO$_2$ adsorption capacity was also determined by a simultaneous TGA instrument (SDT Q600, TA Instruments, New Castle, Delaware, USA). About 10 mg of sorbents was pretreated at 105°C for 1 hr with N$_2$ purge flow at 120 mL/min. After cooling down, the flow was switched to pure CO$_2$ and passed through the crucible at 75 and 35°C respectively. The whole adsorption process lasted about 1.5 hr. The final weight gain was regarded as the CO$_2$ adsorption capacity.

### 2. Result and discussion

#### 2.1. CO$_2$ adsorption capacities

First, the CO$_2$ adsorption amounts at 75°C of modified PEI/SBA-15 with three esters addition (loading content is 5%) were determined in a fixed adsorbent bed and the results are given in Fig. 1. It can be observed that both phosphate-based esters (TEP and BEP) promoted the CO$_2$ adsorption, while TMPA had a slightly negative effect on the amount of CO$_2$ adsorbed. Among them, TEP is the optimal additive, being able to increase CO$_2$ adsorption capacity by 18.8% (82.93 mg-CO$_2$/g-adsorbent at 75°C in 9.5 vol.% CO$_2$/N$_2$). As TEP showed the best effect on the CO$_2$ adsorption capacity by 18.8% (82.93 mg-CO$_2$/g-adsorbent at 75°C in 9.5 vol.% CO$_2$/N$_2$). It can be observed that both phosphate-based esters (TEP and BEP) promoted the CO$_2$ adsorption, while TMPA had a slightly negative effect on the amount of CO$_2$ adsorbed. Among them, TEP is the optimal additive, being able to increase CO$_2$ adsorption capacity by 18.8% (82.93 mg-CO$_2$/g-adsorbent at 75°C in 9.5 vol.% CO$_2$/N$_2$). As TEP showed the best effect on the performance of the adsorbent, the effects of different loading contents of TEP were investigated based on the PEI-SBA-15 adsorbent with the same PEI proportion (45 wt.%), which is shown in the inset figure of Fig. 1. It was found that the amount of CO$_2$ adsorbed increased with increasing TEP loading content and reached its maximum value at 5 wt.% TEP addition. Further increase of the TEP amount lowered the CO$_2$ adsorption capacity. The possible reason is that more surfactant addition would lead the total loaded volume (TEP + PEI) to exceed the pore volume of the SBA-15. Thus the overloading of the surfactant and PEI blocked the tunnels of SBA-15, leading to a decrease in the available surface for amino groups. Therefore, the upper loading content of PEI and the surfactant should be around 50 wt.%.

The textural properties and amine content of the αPEI-βTEP/SBA-15 with fixed loaded content (50 wt.% of PEI + TEMP) are shown in Table 1. From Table 1, it can be seen that the void volume and surface area of the PEI + TEP loaded samples almost vanished compared to the fresh SBA-15, which indicated that all the pore volume of SBA-15 was filled by PEI and TEP, and the loaded amine content exhibited an unsurprising decrease with the decrease in the amount of impregnated PEI. Fig. 2 shows the CO$_2$ adsorbed amounts and amine efficiencies of these above-mentioned absorbents. As seen in Fig. 2, all the surfactant-added materials showed an improvement in comparison with 50PEI/SBA-15, though the promoting effect was not strong due to the decrease of amine content. However, amine efficiency increased from about 0.17 for surfactant-free adsorbent to 0.21 for 43PEI-7TEP/SBA-15. According to the literature (Bollini et al., 2011; Xu et al., 2003), higher loading content of PEI should lead to higher amine efficiency, since two amines are required to bind one CO$_2$ molecule under dry conditions, and increasing the amine loading would result in a rise in amine proximity. As such, this increase in amine efficiency at lower amine loading content could be assumed to be attributable to the enhanced diffusion of CO$_2$ after TEP was added, as suggested by Wang et al. (2012).

#### 2.2. CO$_2$ adsorptive kinetics

To further confirm that TEP had a promoting effect on the dispersion of loaded PEI polymer, we measured the static adsorption rate for CO$_2$ by conducting TG-DSC testing for the adsorbents with/without TEP addition (using 50PEI/SBA-15 and 49PEI-1TEP/SBA-15 as examples) in the pure CO$_2$ condition at 35 and 75°C (see Fig. 3). As shown in Fig. 3, the CO$_2$ adsorption process on PEI-functionalized samples could be divided into two stages, as suggested in the previous studies.

![Fig. 1 - CO$_2$ adsorption amount of samples loaded with 45 wt.% polyetherimide (PEI) with/without 5 wt.% surfactant addition. Inset figure shows the effect of tri(2-ethylhexyl) phosphate (TEP) amount on the CO$_2$ adsorption capacity. The adsorbents were dented as αPEI–βsurfactant/SBA-15 (2-D hexagonal P6mm, Santa Barbara USA), where α and β refer to the weight percentage of PEI and the surfactants, respectively.](image-url)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{Total}$ (cm$^3$/g)</th>
<th>Loaded amine (mmol N/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>617.26</td>
<td>0.91</td>
<td>–</td>
</tr>
<tr>
<td>50PEI/SBA-15</td>
<td>7.69</td>
<td>0.021</td>
<td>10.6</td>
</tr>
<tr>
<td>49PEI-1TEP/SBA-15</td>
<td>7.76</td>
<td>0.025</td>
<td>9.54</td>
</tr>
<tr>
<td>47PEI-3TEP/SBA-15</td>
<td>5.93</td>
<td>0.021</td>
<td>9.02</td>
</tr>
<tr>
<td>45PEI-5TEP/SBA-15</td>
<td>5.16</td>
<td>0.022</td>
<td>9.31</td>
</tr>
<tr>
<td>43PEI-7TEP/SBA-15</td>
<td>6.32</td>
<td>0.018</td>
<td>8.75</td>
</tr>
</tbody>
</table>

$S_{BET}$: the BET surface area calculated from the adsorption branch of the N$_2$ isotherm; $V_{Total}$: the total pore volume calculated at P/P$_0$ = 0.99; PEI: polyetherimide; TEP: tri(2-ethylhexyl) phosphate. The adsorbents were dented as αPEI–βsurfactant/SBA-15, where α and β refer to the weight percentage of PEI and the surfactants, respectively.
First, CO2 transferred from outside the pores to the superficial layer of PEI polymer, which is mainly controlled by molecular diffusion. At this stage, the CO2 adsorption uptake was also the same. Second, CO2 penetrated into the inner-layers of the PEI polymer, where inner diffusion is more important. Thus, the dispersion of PEI molecules had a significant effect at the second stage. Compared with the surfactant-free sample 50PEI/SBA-15, 49PEI-1TEP/SBA-15 showed a higher adsorption rate at the second stage, especially at 35°C. It has been reported that the inner diffusion limitation is stronger at lower temperature (Choi et al., 2009; Xu et al., 2002; Yue et al., 2006), which would imply more severe agglomeration of PEI polymer. As such, these results indicated that the addition of TEP promoted the physical dispersion of PEI inside the tunnels of SBA-15, decreasing the diffusion resistance toward CO2.

2.3. Cyclic performance

As is well known, stable cyclic performance of the adsorbent is another important factor for practical industrial application. To investigate the effect of TEP addition on the multi-cycle behavior of the PEI-impregnated SBA-15 adsorbent, 20 adsorption/desorption cycles were performed for 45PEI-5TEP/SBA-15 and 45PEI/SBA-15 samples. Each cycle was conducted in two stages, with a CO2 adsorption step under 9.5 vol.% CO2/N2 feed gas at 75°C for 30 min and a regeneration step under 99.999% N2 at 105°C for 60 min. The amounts of CO2 adsorbed for the tested adsorbents for each cycle are shown in Fig. 4. It was revealed that 45PEI-5TEP/SBA-15 exhibited an improved cyclic stability in comparison with 45PEI-1SBA-15. For TEP-free samples, the amount of CO2 adsorbed decreased gradually and showed a loss of more than 10% of the initial value after 20 cycles. However, the 45PEI-5TEP/SBA-15 adsorbent exhibited much better reversible CO2 adsorption performance, almost preserving its initial capacity. Wang et al. (2012) argued that the surfactant served as a flexible buffering matrix and could preserve its ability to disperse the PEI molecules during the temperature swing in the adsorption–desorption process. This may be one of the important reasons for the improved cyclic performance of the TEP-containing sample.

Based on the above-mentioned hypotheses, in situ FT-IR was conducted for the CO2 desorption process at 105°C for 60 min after CO2 pre-adsorption at 75°C for 30 min (see Fig. 5). From Fig. 5, it can be seen that after CO2 adsorption, several IR bands appeared corresponding to adsorbed CO2 species. The bands at 3423, 3367 and 3299 cm⁻¹ could be assigned to N–H stretching vibrations (Hiyoshi et al., 2005; Huang et al., 2003; Wang et al., 2009), where the positive band at 3423 cm⁻¹ was caused by the N–H stretch of carbamate (–NHCOO⁻) and the negative bands were caused by the chemical adsorption of CO2 on the amino groups (R-NH2). The bands in the ranges of 3000–2800 cm⁻¹ were due to C–H stretching vibrations (Chang et al., 2003; Su et al., 2010). Gaseous or physically adsorbed CO2 species-related peaks emerged at 2360 and 2341 cm⁻¹ (Bacsik et al., 2011, 2010; Liu et al., 2010; Srikanth and Chuang, 2013; 2012).
Wang et al., 2009). The peak at 3039 cm$^{-1}$ was attributed to ionic NH$_3^+$ stretching (Srikanth and Chuang, 2013). The two broad peaks (2000–2800 cm$^{-1}$) were due to the chemically adsorbed CO$_2$ in the bulk PEI multilayers according to the work of Wang et al. (2009), and the band at 1690 cm$^{-1}$ could be assigned to C=O in carbamic acid (Bossa et al., 2008; Dell’Amico et al., 2003). In our previous study (Liu et al., 2013b), the above-mentioned peaks were found to be less stable than carbamate and assigned to weakly adsorbed CO$_2$ species. Additionally, the bands in the ranges of 1320–1635 cm$^{-1}$ were attributed to carbamate species (Bacsik et al., 2010, 2011) (RNH$_3^+$ at 1635 and 1500 cm$^{-1}$, COO$^-$ at 1567 cm$^{-1}$ combined with NCOO$^-$ at 1411 and 1320 cm$^{-1}$). Fig. 5 also shows, from top to bottom, the IR curves recorded at 1, 3, 5, 7, 10, 15, 20, 30, 40, 50, and 60 min during the desorption process in pure He flow at 105°C, respectively. It can be seen from Fig. 5 that with He purge at 105°C, all the corresponding bands are reduced, and the bands related to weakly adsorbed CO$_2$ species almost vanished after 60 min of desorption for both samples. However, in the region of carbamate species, the desorption behaviors for the two samples were very different. The bands due to carbamate species could be almost completely desorbed for 45PEI-STEP/SBA-15 in 30 min, while these absorption bands could still be observed for the TEP-free sample even after a 60 min thermal desorption treatment. This further confirmed that TEP addition could be beneficial to the CO$_2$ diffusion in PEI/SBA-15.

2.4. Thermal stability

In addition, the thermal stability of the samples was also evaluated by conducting TG-DSC experiments from 30 to 800°C in an air atmosphere. As shown in Fig. 6, the TEP-added samples all exhibited an increase in thermal stability, as the first decomposition peak increased by around 15°C. It was reported that higher dispersion of PEI would result in lower thermal stability (Liu et al., 2013a; Son et al., 2008; Xu et al., 2003). The enhancement in thermal stability by TEP addition
observed herein might be due to two main reasons. The first reason is the higher thermal decomposition temperature of TEP. Second, TEP could have a binding effect on the loaded PEI, which needs further confirmation. This finding regarding the enhanced thermal stability could somewhat improve the cyclic performance due to lower degradation of the loaded amine with thermal cycling.

3. Conclusions

In this study, the effect of adding phosphorus-containing surfactants on the adsorptive performance of modified PEI/SBA-15 for CO₂ was investigated. The experimental results on a fixed bed in 9.5 vol.% CO₂ at 75°C revealed that TEP and BEP could improve the CO₂ adsorption capacity by around 19% and 9%, respectively. It was then found that 5 wt.% was the optimal addition content for 45PEI-9TEP/SBA-15. Further investigation for fixed total loading content (50 wt.%) proved that the TEP-added samples exhibited highly improved amine efficiency, which confirmed that TEP enhanced the dispersion of PEI in the tunnels of SBA-15. In addition, the adsorptive kinetic results concluded that the CO₂ adsorption rate indeed was enhanced after TEP addition, especially for the lower temperature condition (35°C). Furthermore, the adsorption/desorption cyclic performance was tested and the results showed that TEP also had a positive effect. The main reason for the improvement was attributed to the enhancement of CO₂ diffusion with TEP addition. TEP acted as a surfactant in the samples, improving the dispersion of the PEI in the tunnels of the support SBA-15, so that more active amine sites were exposed at the gas-solid interface, decreasing the diffusion resistance of CO₂, which could be confirmed by the in-situ DRIFT results. In addition, the DSC curves confirmed that the TEP-modified adsorbent had higher thermal stability, which may also benefit the adsorption/desorption cyclic performance to some extent.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jes.2015.04.025.

References


