Carbon dioxide capture using amine functionalized silica gel

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Commercially available silica gel is chemically modified for carbon dioxide capture. Calcinated silica gel of certain particle size functionalized with amine using two different methods, wet impregnation and grafting via silane chemistry has been employed as a porous media. The prepared material is characterized by Fourier transform infrared, scanning electron microscopy, energy dispersive analysis of X-rays, thermogravimetry and N\textsubscript{2} physisorption techniques. Gas uptake measurements have been carried out to ascertain the CO\textsubscript{2} capture capacity of the amine functionalized material. The experiments have been carried out at moderate pressure and temperature range to ascertain its potential for easy scale up.

Keywords: Carbon dioxide capture, Amine functionalized silica gel, Poly(ethyleneimine), Wet impregnation, Grafting, Silane chemistry

Potential impact of green house gas like carbon dioxide on climate has attracted great attention in recent years and research community as a whole is looking to develop strategies for the reduction of carbon dioxide (CO\textsubscript{2}) emissions.\textsuperscript{1} Coal based thermal power plant is one of the major source of electricity generation in India and will continue to dominate for next few decades. CO\textsubscript{2} capture and separation from flue gas and subsequent sequestration have been considered a major solution to control the anthropogenic emission of CO\textsubscript{2}.\textsuperscript{2-4} The partial pressure of CO\textsubscript{2} coming out of such power stations is significantly low and most mature approach is to absorb the CO\textsubscript{2} component from the flue gas with amine based chemical solvents, resulting in bicarbonate and carbamate formation.\textsuperscript{5-7} CO\textsubscript{2} capture by physical adsorption is an alternate approach. Activated carbon\textsuperscript{8} and zeolites\textsuperscript{9-11} have been used as CO\textsubscript{2} adsorbents in a pressure swing/temperature swing approach. Membrane separation processes which include polymeric membranes, microporous membranes and palladium membranes\textsuperscript{12-14} physically separate one gas from another and this approach has also been applied for CO\textsubscript{2} capture and separation from flue gas. Amines immobilized mesoporous silica adsorbent has attracted great attention due to its high CO\textsubscript{2} capture capacity and separation efficiency.\textsuperscript{15}

In the present study, two types of silica supported amine sorbents have been investigated; one in which covalent bond is formed between solid support and the amine and the other where, amine-containing polymers or oligomers, such as polyethylenimine (PEI) or oligoethylenimine is loaded by a simple wet-impregnation method.\textsuperscript{11, 16-18} In these methods, amines are loaded in to the pores of mesoporous substrate leading to high dispersion of amines and thus better CO\textsubscript{2} adsorption performance.\textsuperscript{16} The following porous silica supported materials have been investigated: SBA-12,\textsuperscript{19} SBA-15,\textsuperscript{20-30} SBA-16,\textsuperscript{31} MCM-41,\textsuperscript{32-34} MCM-48,\textsuperscript{35-37} KIT-6,\textsuperscript{38} HMS,\textsuperscript{39} mesocellular silica foam,\textsuperscript{40} silica monolith\textsuperscript{41} and mesoporous silica microsphere.\textsuperscript{42}

In the present work silica gel, a porous material was used as an inexpensive support.\textsuperscript{43} Three commercially available silica gels with different particle sizes were used for initial screening, of which the smallest particle size silica gel (230-400 mesh) was chosen for amine functionalization.\textsuperscript{43} The objective of this study is to develop the amine enriched sorbents for the capture of CO\textsubscript{2} gas using inexpensive and commercially available silica gel as a support. Focus is on the scale up potential of the process, idea is to choose a material and its synthesis process which can be scaled up easily and does not require many unit operations. In this study, the silica gel (230-400 mesh)-supported poly(ethyleneimine) adsorbent (SG-PEI) and amine grafted silica gel (SG-APTS) were prepared. The prepared material was characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), energy
dispersive analysis of X-rays (EDAX), thermogravimetry (TG) and \( \text{N}_2 \) physisorption techniques. Gas uptake measurements were carried to ascertain the \( \text{CO}_2 \) capture capacity of the material used.

**Materials and Methods**

Carbon dioxide gas and gas mixture (15 mol\% \( \text{CO}_2 \)/85 mol\% \( \text{N}_2 \)) with a certified purity of more than 99.9\% were supplied by Deluxe Industrial Gases, Pune, India. Silica gels with \( \geq 99 \% \) purity (LR grade) were purchased from Rankem Ltd, Pune, India. (3-Aminopropyl) trimethoxysilane (APTS) with minimum 98\% purity and poly-ethyleneimine (PEI) having molecular weight of 1300 were purchased from Sigma Aldrich, Bangalore, India. All the materials were used without further purification.

**Preparation of amine grafted silica gel (SG-APTS) via silane chemistry**

Amorphous silica gel (230-400 mesh) was heated at 723 K to give silica substrate with silanol group (hydroxyl group) on the surface. The SG-APTS porous material was synthesized based on the method reported by Knowles *et al.*\(^{44}\) and Chang *et al.*\(^{45}\) Approximately, 1 g of pre-dried silica gel was dispersed in 50 mL toluene and treated with 10 mL of (3-aminopropyl)trimethoxysilane (APTS) after refluxing at 358 K for 6 h. The crude product was filtered, washed with 20 mL of ethanol through PTFE filter paper having 0.2 \( \mu \text{m} \) pore size and then dried at 343 K for 24 h under vacuum to produce amine grafted silica gel.

**Preparation of amine loaded silica gel (SG-PEI) by wet-impregnation method**

The SG-PEI porous material was prepared by a wet-impregnation method.\(^{36,38}\) In this preparation, about 1.0 g of PEI was dissolved in 20 mL of methanol under stirring for 60 min to make a PEI/methanol solution. The silica gel (1.0 g) after vacuum drying at 373 K was added to the PEI/methanol solution. The slurry was continuously stirred at room temperature for about 6 h, allowing the methanol in the slurry to evaporate. After removing methanol, the sample was further dried in a vacuum of 0.001 MPa for 12 h at 313 K.

**Characterization**

The BET surface area, pore volume and pore diameter of the samples were measured by the \( \text{N}_2 \) adsorption-desorption at 77 K using the Quantachrome autosorb automated gas sorption system. Pore volumes were calculated on the basis of the adsorbed \( \text{N}_2 \). Grafting/functionlization were confirmed by FTIR (Perkin Elmer) spectra obtained in the range of 4000-400 cm\(^{-1}\). Thermal stability of SG-PEI and SG-APTS samples were evaluated by using STA 7000 thermogravimetry analyzer, where 15 mg of the sample was heated at a rate of 283 K/min from room temperature to 873 K under \( \text{N}_2 \) environment. The SEM images (morphological studies) were obtained on a FEI Quanta 200 3D dual beam ESEM, operating at 20 kV while EDAX was used for elemental determination.

**Experimental setup and procedure**

Schematic of the apparatus is shown in Fig. 1. It consists of a 10 mL SS-316 high-pressure reactor (R) connected with a supply vessel and an online gas chromatograph (GC). Proper arrangement was made for evacuating the reactor with a vacuum pump (model N86KT.18, KNF Lab, India) and a separate high pressure vent. All pressure measurements were made with pressure transducers (WIKA make), with a range of 0-16 MPa and accuracy of less than 0.075\% of the span. The reactor was immersed in a water bath (Julabo-F34) containing a 50/50 (wt\%) methanol/water mixture which maintained the temperature in the reactor constant. A suitable data acquisition system recorded the temperature and pressure of the reactor with respect to time.

The dry adsorbent (0.5 g) was placed inside the reactor and evacuated at 0.01 MPa for 10 minutes. The reactor was pressurized with \( \text{CO}_2 \) at a desired pressure (1 MPa, 2.5 MPa and 3.5 MPa) and temperature inside the reactor was kept constant using a water bath. Time zero of the reaction was the time at which the sample was exposed to \( \text{CO}_2 \) and the change in pressure inside the reactor was monitored and...
recorded every 5 seconds. A sophisticated data acquisition system (DAQ) with a computer was installed to record and reproduce the gas uptake data at the end of the experiment. The total number of moles of gas consumed from the gas phase was calculated by Eq. 1 with the help of pressure drop data collected through DAQ. When gas uptake measurement was being conducted for a gas mixture, a small sample of gas was taken at constant interval and analyzed via GC (Shimadzu-2014, equipped with a thermal conductivity detector and shin carbon packed bed column) to monitor gas phase composition.

\[ n = \frac{PV}{ZRT} \]  \hspace{1cm} \text{... (1)}

In Eq. (1), \( Z \) is the compressibility factor calculated by Pitzer’s correlation, \( P \) is pressure in kPa, \( R \) is gas constant in suitable unit, \( T \) is temperature in Kelvin, \( V \) is the volume of reactor in liters and \( n \) is the number of moles of gas present in the system.

To evaluate the separation efficiency of the amine loaded silica gel, an experiment was conducted using flue gas (\( \text{CO}_2/\text{N}_2 \)) with a 15 mol% of \( \text{CO}_2 \) and the rest \( \text{N}_2 \) at 3.5 MPa and at 323 K. The \( \text{CO}_2 \) recovery or split fraction (S. Fr.) was calculated by using Eq. (2).\(^\text{37}\)

\[ \text{S. Fr.} = \frac{n^\text{consumed}_{\text{CO}_2}}{n^\text{Feed}_{\text{CO}_2}} \]  \hspace{1cm} \text{... (2)}

where \( n^\text{consumed}_{\text{CO}_2} \) is the number of moles of \( \text{CO}_2 \) consumed from the gas phase and \( n^\text{Feed}_{\text{CO}_2} \) is the number of moles of \( \text{CO}_2 \) in the feed gas. The separation factor (S.F.) was determined from the following Eq. (3).\(^\text{37}\)

\[ \text{S. F.} = \frac{n^\text{gas}_{\text{CO}_2} \times n^\text{consumed}_{\text{N}_2}}{n^\text{consumed}_{\text{CO}_2} \times n^\text{gas}_{\text{N}_2}} \]  \hspace{1cm} \text{... (3)}

where \( n^\text{gas}_{\text{CO}_2} \) and \( n^\text{gas}_{\text{N}_2} \) are the number of moles of \( \text{CO}_2 \) and \( \text{N}_2 \) in the gas phase at the end of the experiment and \( n^\text{consumed}_{\text{N}_2} \) is the number of moles of \( \text{N}_2 \) consumed by the material. We know that the total pressure of a gas mixture is the sum of the partial pressures of each individual gas in the mixture. In this work, the partial pressures of the individual gases such as \( \text{CO}_2 \) and \( \text{N}_2 \) were calculated by multiplying the absolute pressure with volume fraction of gas component (15 % \( \text{CO}_2 \)/85 % \( \text{N}_2 \)). The final \( \text{CO}_2 \) uptake for flue gas was calculated with the help of partial pressure term.

**Results and Discussion**

**Characterization**

The silica gel surface is quite complex and contains more than one type of hydroxyl groups. Out of the three types of hydroxyl group, the first one is a single hydroxyl group attached to a silicon atom which has three siloxane bonds connecting it to the gel matrix. The second one is two hydroxyl groups attached to the same silicon atom, which in turn is connected to the matrix by two siloxane bonds. These twin hydroxyl groups are called geminal hydroxyl groups. The third one has three hydroxyl groups attached to a silicon atom, which in turn are connected to the silica matrix by only a single siloxane bond. The interaction between the amine functionalized silica surface and \( \text{CO}_2 \) molecules is thought to result in the formation of ammonium carbamates under anhydrous conditions (Fig. 2) and ammonium bicarbonate and carbonate species in the presence of water.\(^{46-51}\) In the case of unmodified SG, the silanols are the active sites for \( \text{CO}_2 \) uptake. However as shown in Fig. 2, the functionalized materials contain amine functionalities which become active site for \( \text{CO}_2 \) adsorption, resulting in formation of carbamate. In the present study functionalization of silica gel was confirmed by FTIR spectra, as shown in Fig. 3a.

The silica gel (230-400 mesh) and amine loaded silica gel (SG-PEI & SG-APTS) were characterized by FTIR spectroscopy. The IR spectra of silica gel showed bands in the region from 465 to 453 cm\(^{-1}\) due to Si-O bonds\(^{52}\) (not shown in the figure), 801, 802 cm\(^{-1}\) due to Si-O-Si symmetric vibrations\(^{33}\) and a broad band in the range of 3500-3460 cm\(^{-1}\) attributed to hydroxyl group (Si-OH)\(^{54}\) on the surface of silica gel. The insets in Fig. 3 (b and c) show the presence of PEI in silica gel. In Fig. 3c, the two bands appearing at 2955 and 2835 cm\(^{-1}\) represent CH stretching of PEI. The two distinct bands as shown in Fig. 3b at 1476 and 1569 cm\(^{-1}\) are due to asymmetric and symmetric bending of primary amine (NH\(_2\))\(^{54}\). The band at 1654 cm\(^{-1}\) may be assigned to bending of secondary amines in PEI. The inset (d) in Fig. 3...
shows the presence of APTS in silica gel with a band at 692 cm\(^{-1}\) confirming the presence of Si-C bond of APTS. The broad band at \(~3260\) cm\(^{-1}\) may be attributed to amine N-H stretching vibration in amine loaded silica gel.

Thermogravimetric technique has been used to determine the amount of PEI and APTS loaded into the porous silica gel via both the methods explained above. Fig. 4 represents the weight loss profile with respect to temperature in pure calcinated silica gel, PEI loaded silica gel and APTS loaded silica gel. In the case of SG-PEI, the TG curve clearly shows the two main regions of weight loss, out of which first weight loss at 373 K is attributed to desorption of moisture and other gases. In the temperature range of 423-723 K, a sharp change in the weight loss is observed for SG-PEI, due to the combustion of organic substrate (PEI), while in the case of silica gel
and SG-APTS, the weight reduction is marginal and changes gradually. In the current temperature range, weight loss for SG-PEI is ~45% whereas for SG-APTS the weight loss is only ~10%. If the moisture and adsorbed gases are excluded from original weight, then loading amount of PEI and APTS can be calculated as ~25% and 6%, respectively. It has been observed that in the current study about 30% of PEI is lost during the impregnation process.55

SEM and EDAX images of all the three types of silica gels, i.e., commercial silica gel, APTS loaded and PEI loaded are shown in Fig. 5(a, b and c), respectively. It is observed that there is no significant difference in the morphology of the silica gels; dark surfaces are mostly due to presence of amine group on silica gels surface. Fig. 5(c) shows slight agglomeration of PEI on the surface of silica gel particle; however most of the PEI is present inside the pores.56 It can be said that in both the processes of attaching amine functionality to the silica gel, significant modification of silica gel surfaces was not observed. EDAX measurements (Fig. 5) show the elemental analysis (wt%) and as seen in the Fig. 5(a), only Si and O are present (silica gel). In amine loaded silica gel (Fig. 5(b and c) the presence of N and C can be seen clearly, albeit in different amounts. About 14 wt% nitrogen and ~50 wt% carbon content were identified in the case of PEI loaded silica gel and ~4 wt% N and ~25 wt% C in APTS loaded silica gel. Low concentrations of nitrogen in SG-APTS and SG-PEI confirm the poor loading of amine precursor on to the surface which more or less matches with the observation made through SEM images.

The nitrogen adsorption/desorption isotherms at 77 K of the silica gel and amine loaded silica gels are shown in Figs 6a, 6b and 6c, respectively. The isotherms classified as the type IV adsorption/desorption as defined by IUPAC give useful information through their hysteresis loops. Type IV isotherms exhibit a hysteresis loop, i.e., the adsorption and desorption isotherms do not coincide over a certain region of external pressures. The type IV isotherm is typical for mesoporous adsorbents. At low pressures, first an adsorbate monolayer is formed on the pore surface, which is followed by the

Fig. 5 — SEM images and elemental status (inset EDAX) of (a) calcinated silica gel, (b) APTS loaded silica gel, and, (c) PEI loaded silica gel.
multilayer formation. Table 1 lists the BET specific surface area (m$^2$/g), average pore diameter (nm) and pore volume (cc/g) of silica gel and amine loaded silica gels. The BET surface area and pore volume of commercial silica gel are 402 m$^2$/g and 0.56 cc/g, respectively. After amine loading, the surface area as well as pore volume decrease significantly (~70 m$^2$/g and 0.13 cc/g, respectively), which is due to the filling of pores with PEI and APTS (Fig. 6(d and e)).

**Table 1** — Physical properties of silica gel (230-400 mesh) and amine loaded silica gel with CO$_2$ adsorption capacities at different operating pressures and constant temperature of 275 K

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Pore dia. (nm)</th>
<th>Pore vol. (cc/g)</th>
<th>Surface area (m$^2$/g)</th>
<th>CO$_2$ capacity (mg CO$_2$/g adsorbent) at different pressures (MPa)</th>
<th>Total consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG</td>
<td>5.6</td>
<td>0.56</td>
<td>402</td>
<td>35.2 35.2 75.2</td>
<td>146.2</td>
</tr>
<tr>
<td>SG-PEI</td>
<td>7.1</td>
<td>0.13</td>
<td>74.2</td>
<td>39.6 75.2 88</td>
<td>206.8</td>
</tr>
<tr>
<td>SG-APTS</td>
<td>6.9</td>
<td>0.47</td>
<td>270</td>
<td>39.6 30.8 79.2</td>
<td>149.6</td>
</tr>
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</table>

Gas uptake measurements

In the current study three different silica gel of different particle size and almost same pore sizes were identified and used for CO$_2$ adsorption studies. Typically a gas uptake measurement at 3.5 MPa and 275 K were performed and pressure drop with respect to time was recorded (Fig. 7). By using Eq. 1, the number of moles of CO$_2$ consumed after 100 minutes

Fig. 6 — Nitrogen adsorption-desorption isotherms of (a) silica gel, (b) APTS loaded silica gel, and, (c) PEI loaded silica gel. Pore size distribution plots: (d) BJH adsorption, and, (e) BJH desorption of silica gel and amine grafted silica gel. [1, silica gel; 2, SG-APTS; 3, SG-PEI].

Fig. 7 — Comparison of CO$_2$ adsorption capacities of three types of silica gel at operating pressure of 3.5 MPa and constant temperature of 275 K. [1, 60-120 mesh; 2, 100-200 mesh; 3, 230-400 mesh].
of experiment were calculated and are reported in Table 2. It was observed that the CO$_2$ adsorption capacity of these silica gel particles increases with decreasing particle size. As shown in Fig. 7, the smaller particle size (40-65 µm) had the largest adsorption capacity at 275 K. The increase in gas uptake for smaller particle size can be attributed to the higher surface area (m$^2$/g) in smaller particle adsorbent. Based on this result, silica gel with smaller particle size (230-400 mesh) was chosen for amine loading to improve the CO$_2$ capture efficiency.

Nine different gas uptake measurements were performed (as discussed above) at three different pressures and constant temperature with each of the three systems as reported in Table 1. Figure 8 shows single component isotherms for CO$_2$. Adsorption of CO$_2$ is plotted as a function of pressure upto 3.5 MPa capacities for each of the three systems studied during this work with commercial silica gel (230-400 mesh) and amine grafted silica gel. The experiments were performed at three different pressures of 1, 2.5 and 3.5 MPa and at isothermal condition, 275 K. It was observed that with increasing pressure, adsorption capacity increases linearly. As seen, CO$_2$ adsorption capacities are maximum for SG-PEI with a total CO$_2$ consumption of 206 mg/g-adsorbent at 3.5 MPa. It was also observed that at lower pressure of 1 MPa, the CO$_2$ adsorption capacities in the three systems were very similar. Chang et al. in their studies suggested that the amount of CO$_2$ adsorbed increases with increasing amine loading. As per the characterization carried out in this study, the amount of amine loading was found to be maximum for SG-PEI, thus resulting in better CO$_2$ adsorption.

Figure 9 shows the comparison of CO$_2$ uptake in silica gel (230-400 mesh) compared to PEI loaded silica gel. Silica gel by itself has a maximum capacity of ~140 mg-CO$_2$/g-silica gel. However, in PEI loaded silica gel no such saturation was seen for up to ~3 h of gas uptake measurement. It is important to note that chemical reaction in presence of amine functionality is the main factor which drives further gas uptake in the case of SG-PEI as compared to silica gel alone. It is quite clear that SG-PEI has outperformed SG-APTS for CO$_2$ capture potential, which is no better than silica gel alone. However, poor performance of SG-ATPS needs an explanation which is beyond the scope of current work.

An experiment was conducted using flue gas (15 % CO$_2$ and 85 % N$_2$ mixture) to evaluate the separation efficiency (experimental conditions shown in Table 3) of the SG-PEI system. The gas uptake measurement shows CO$_2$ adsorption in tune of 245 mg-CO$_2$/g-adsorbent, which compares quite well with the adsorption capacities reported in the literature. Also, split fraction as well as separation factor of CO$_2$.

<table>
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<tr>
<th>Table 2 — Comparison of the CO$_2$ adsorption capacities of various commercial silica gel at 3.5 MPa and 275 K after 100 minutes</th>
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<tbody>
<tr>
<td>Adsorbent</td>
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<tr>
<td>-----------</td>
</tr>
<tr>
<td>Silica gel (60-120 mesh)</td>
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<td>Silica gel (100-200 mesh)</td>
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<td>Silica gel (230-400 mesh)</td>
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Fig. 8 — Total CO$_2$ consumption with respect to pressure at 275 K in silica gel and amine loaded silica gels. [Experimental data has been fitted linearly. 1, silica gel; 2, SG-APTS; 3, SG-PEI].

Fig. 9 — Comparison of CO$_2$ adsorption capacities of silica gel (230-400 mesh) and amine loaded silica gel (SG-PEI) at 3.5 MPa and 275 K. [1, SG (230-400 mesh); 2, SG-PEI].
Compared to N₂ (for flue gas) needs to be studied for commercial utilization of these materials for practical applications. Split fraction or CO₂ recovery was calculated using Eq. 2 and was found to be around 0.87, indicating that ~87% of CO₂ in the feed gas is separated in the process. Separation factor as defined by Eq. 3 can be used to identify the selectivity of SG-PEI for CO₂ over N₂ and was found to be ~530. Such a high value of separation factor would indicate selective chemical adsorption of CO₂ on amine functionalized silica gel.

Table 3 compares the results obtained in this work with available literature. It can be seen that amine-impregnated silica monolith has the maximum reported capacity of 188 mg CO₂/g adsorbent. Similarly, for mesoporous alumina and KIT-6, the CO₂ uptake is less as compared to the present work. One interesting approach, where mesoporous capsules were used for CO₂ capture, resulted in better CO₂ uptake. It is important to note that higher loading of amine is essential for better CO₂ capacity and the focus of future work will be to increase the amine loading.

Conclusions
Amine loaded silica gel was successfully developed for CO₂ capture and separation. The characterization results showed that the loading of amine was higher in synthesized SG-PEI as compared to SG-APTS. It was found that the amine loaded silica gel shows significant CO₂ uptake as compared to bare silica gel. Irrespective of CO₂ capture efficiency, the comparatively simpler process of attaching amine functionality in the case of SG-PEI (compared to SG-APTS) makes it an ideal candidate for large scale application. Higher amine loading, which is essential for better CO₂ adsorption, can be obtained by using a silica gel of higher pore volume and higher surface area compared to the silica gel studied in this work.

The use of commercial silica gel for CO₂ capture is more economical as compared to other mesoporous materials and has scale up potential for commercial applications.

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References