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Amine Impregnated Porous Silica Gel Sorbents Synthesized from Water-Glass Precursors for CO$_2$ Capturing

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Abstract

In this work, porous silica gel-solid beads have been made from economically affordable water-glass precursors via sol-gel nano casting technique. A stable nanometric silica sol was prepared first from water glass and studied for surface potential and sol to gel transition. A free-flow, injectable gel was obtained upon aging the sol which was then assembled into spherical silica beads in a chemical bath. A surface area of 304.7 $m^2 g^{-1}$ was obtained for water glass derived silica gel beads. These gel beads were impregnated with 3-aminopropyltrimethoxysilane (APTMS) and polyethylenimine (PEI) active functional groups at different percentages for turning the gel beads as sorbents for CO_2 gas adsorption. The effect of amine loading on the thermal stability, morphology as well as porosity was studied and was correlated with CO_2 adsorption values. Depending upon the amount of amine loaded in the gel support CO_2 uptake was found varied. These amine modified silica gel porous adsorbents showed CO_2 adsorption capacity at temperatures as low as 100 ^{o}C; samples modified with 15 wt% PEI had CO_2 adsorption capacity of 1.16 mmol g^{-1} at 50 ^{o}C.

1. Introduction

A profound solution to curtail the ever rising atmospheric temperature is to minimize the emission of harmful green house gases in to the atmosphere by efficiently managing the release of CO_2 gas. At present, selective removal of CO_2 from flue gases using liquid amines have been widely employed [1-4]. However, liquid amines lose adsorption capacity through amine degradation and therefore sorbent make up cost could add up costs to the system [5].This, in addition to the high regeneration costs of the amine sorbent is a major set-back for the wide deployment of the separation technology. Newer processes such as membrane separation and chemical looping combustion are also being considered for CO_2 capture. However, large scale deployment of these new systems may take another decade. Meanwhile, CO_2 adsorption using solid sorbents is in fact considered as the most practical option because it offers the potential of lowering energy costs for regeneration compared to liquid amine scrubbing technology [6].

Since compositions and temperatures of industrial flue gases could vary, currently there is huge interest in synthesizing solid adsorbents that could perform well under low CO_2 partial pressures and temperatures ~100 ^{o}C. High surface area porous materials impregnated with active amine functional groups are functional materials designed and studied extensively as solid sorbents for CO_2 adsorption [7]. Carbon materials like graphene, zeolites, metal organic frameworks and alkali metal carbonates are also fastly emerging as potential CO_2 adsorbents [8-10]. A large number of porous materials like MCM- 41, SBA-15, porous silica, clays etc have been reported in the literature; CO_2 adsorption on such porous materials is usually governed by physical adsorption and therefore capacity and selectivity values are generally poor at elevated temperatures [11-15]. Recently, such porous materials grafted with amine functionality or impregnated with amine containing molecules are also reported and found to exhibit better selectivity, and increased CO_2 adsorption capacity. The basic amine

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reacts with acidic carbon dioxide and form carbamates or bicarbonates depending on the amine (primary or secondary) and moisture content [16-18].

Aerogel, an ultra-lightweight, multi-porous inorganic substance formed via 3-D gel network from which a gel-liquid is selectively removed via supercritical drying is a promising solid-sorbent for CO_2 sorption and storage [19]. SiO_2 aerogel are novel materials with characteristics of high surface area, high pore volume and low density. These materials also facilitate fabrication of shapes such as micro/ macro beads, foams and gel monoliths. They have been widely used in the fields of thermal insulation, catalysis and sorption [20].The high cost of aerogel made using alkoxide precursors and their fabrication via super critical drying actually limits their industrial applications. Recently, silica aerogel were synthesized at ambient pressure via solvent exchange and surface modification of wet gels [21-24]. Also, synthesis using cheap silica precursor is suggested in the literature [25]. Sodium silicate, conventionally known as water-glass, is an easily affordable silica source for industrial manufacturing of porous silica gels resembling the aerogel.

Herein we report the synthesis of porous, water-glass silica gel beads (macro spheres) via nano casting followed by ambient pressure drying. A simple sol gel technique was employed to obtain the silica gel. Beads formed via nano-casting were solvent exchanged to remove the pore liquid and treated with silanol group to control cracking and drying shrinkage. Thus prepared spherical silica beads were finally modified with amines, 3-aminopropyltrimethoxysilane (APTMS) and polyethylenimine (PEI). The effect of amine loading and its efficiency in the absorption of CO_2 gas was studied and correlated with respect to amine functionality and pore structure of the adsorbent.

2. Experimental

2.1. Materials and Methods

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2.1.1. Materials

Sodium silicate solution (Na_2O 7.5-8.5%, SiO_2 25.5-28.5%) purchased from Merck, USA was used as the silica precursor. Acetic acid (BDH Chemicals, US) was used as acid catalyst. Tetraethylorthosilicate (TEOS) used as silylating agent was purchased from Alfa Aesar, UK. The aerogel beads were modified with 3-(trimethoxysilyl) propylamine (APTMS) and Polyethylenimine (PEI) both purchased from Aldrich Chemicals, USA. Distilled water was used as solvent in all cases.

2.1.2. Synthesis of water-glass beads

Silica gel was prepared via hydrolysis and polycondensation of sodium silicate precursor. For the preparation of silica sol, sodium silicate and acidified water was mechanically mixed until the solution became homogenous. The pH of the solution was adjusted to ~4 using acetic acid [26]. It was then injected through an orifice in to an ammonia bath having a kerosene separation top-layer. The presence of kerosene layer induced surface tension hence forcing the sol to form a spherical granular shape. The spheroid attained gelation when it entered the ammonia bath due to the increase in the pH. The process resulted in good, spherical beads which were kept in the reaction bath for 3 h. The beads were then repeatedly washed with distilled water to remove the sodium ions. The wet gel beads were subjected to solvent exchange process four times in isopropanol medium. The gel beads were finally surface modified using a TEOS/ hexane reactant mixture prepared in 1:1 molar ratio. The excess TEOS was removed using fresh hexane after which the beads were ambient pressure dried at 55 °C to evaporate the solvents [25].

2.1.3. Synthesis of amine-functionalized silica beads

Ethanolic amine solution was prepared first with APTMS and PEI. Two separate batches of ethanol solution containing 5 and 15 wt % PEI, and 2 wt % APTMS were

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prepared. A wet impregnation method was employed. On finishing the solvent exchange process detailed earlier, the silica gel spheroids were kept in these amine solutions for 24 h to allow the surface hydroxyl groups present in gel silica to react with the amino groups resulting in amine grafting. A mild mechanical shaking was given to the reactant solution during the impregnation step. At the end, isopropanol washing was carried out to shed-off any un-reacted amine.

2.1.4. Characterization

Sol-gel transition of water glass derived silica sol was monitored via viscosity measurements using Anton Paar Modular Compact Rheometer (MCR 102) at constant shear rate using a plate-plate system. Zeta potential and particle size distribution of the water glass derived silica particulate sol were performed with a Zetasizer Ver. 6.20 (Malvern Instruments Ltd., UK). The structural properties of gel supports before and after amine grafting were characterized by FT-IR (IR Prestige21 SHIMADZU, Japan) spectroscopy. For IR analysis, the standard transmission technique was followed for which powdered samples mixed with KBr were used for measurements. The surface morphology of the dried gel support as well as the bulk nature of particle assembly during nano-casting was studied using Scanning Electron Microscope (JEOL JSM-5600LV). The Brunauer-Emmett-Teller (BET) model was used to determine the surface area of the beads based on the amount of N_2 gas adsorbed using Micromeritics Gemini 2375 surface area analyzer. Prior to N_2 adsorption measurements, the samples were degassed by evacuation at 200 ^{o}C temperature under N_2 atmosphere. The thermal stability of the silica microspheres with and without amine grafting was examined using thermogravimetry (TG) apparatus (Perkin Elmer STA 6000, Netherlands). For this, the samples were heated in air atmosphere and the TG was taken from room temperature to 1000 ^{o}C at a controlled heating rate of 10 ^{o}C/ min. The same instrument was also used for the gravimetric CO_2 adsorption studies at 50 ^{o}C with a N_2 flow rate of 49 mL/ min and a CO_2

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flow rate of 50 mL/ min. Volumetric CO_2 adsorption studies were performed using a BEL (Belsorp max, BEL JAPAN INC) gas analyser up to the pressure of 1 bar and in the temperature range 5 ^{o}C -100 ^{o}C.

3. Results and discussion

3.1. Zeta potential and particle size distribution

Results on the stability of water-glass derived silica sol as well as its hydrodynamic diameter as observed from the zeta potential analysis and DLS measurements are presented in Fig.1(a & b). Zeta potential curve in Fig.1(a) shows clearly a peak at -27.8 mV indicating that sol particles exhibited negative surface charges due to surface hydroxyl groups. The particle size distribution curve in Fig.1(b) indicates the water glass based silica sol has particle size distribution in the range 200-400 nm. The average hydrodynamic particle size was ~297 nm. This is a comparatively high value for nanosized silica prepared through conventional sol-gel technique. Acid catalyzed alkoxide derived silica sol generally produces spherical SiO_2 nanoparticles with average particle diameter in the order of 30 to 50 nm depending upon the pH. Alkoxide precursor is in fact more reactive and facilitates growth of atomic scale parent seed nuclei that ultimately helps to reduce the particle size [27]. In water glass precursor, acid stabilization produces exothermic reaction. As a result of that large size primary crystallites grow upon hydrolysis and thus increase the final particle size. However, the negative zeta potential confirms that these silica particles are also equally stable and size has not affected their stability. This stable sol was transformed to polymeric gel via condensation reactions as shown in reaction 1. The polycondensation process results in the formation of silica network through –Si-O-Si- chemical linkages finally yielding a rigid, non-fluid gel mass consisting of silica particles assembled in a 3-D network where pores are filled with the solvent. As shown

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in the reactions detailed in equations (1 and 2), thus formed silica gel frameworks contain excess surface -OH groups which enable them for any suitable chemical modifications.
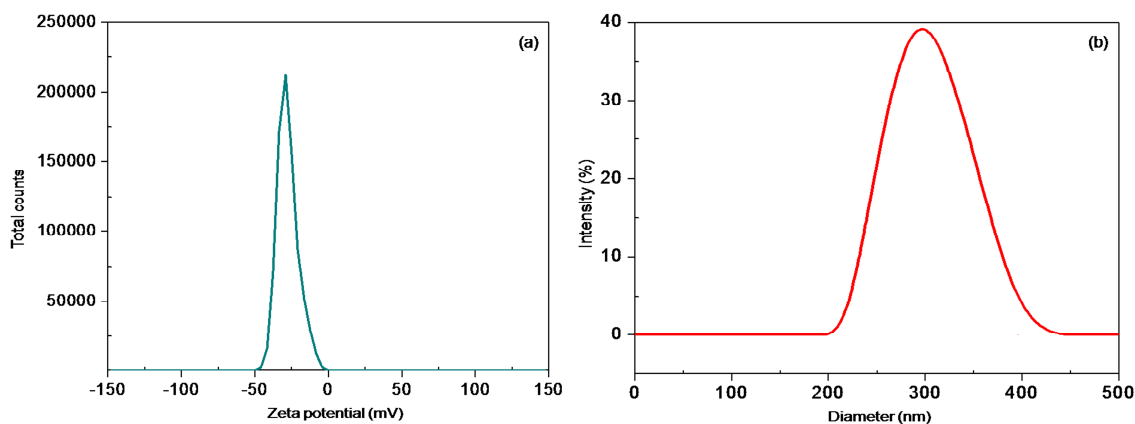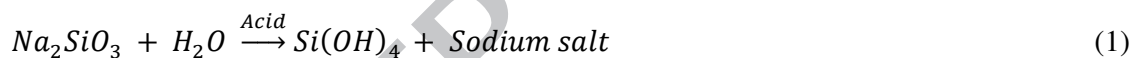

Fig. 1. (a) Zeta potential and (b) size distribution curve for silica sol prepared at pH 4.
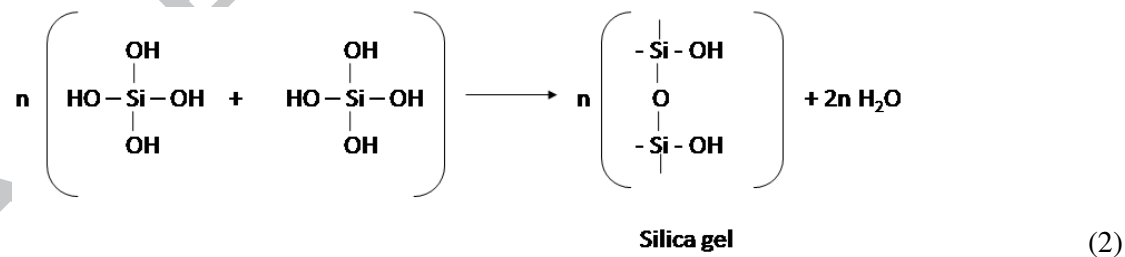
The envisaged reaction mechanism is as follows:

Hydrolysis:

$$Na_2SiO_3 \ + \ H_2O \ \xrightarrow{Acid} \ Si(OH)_4 \ + \ Sodium \ salt \tag{1}$$

Sodium silicate   Silicic acid

Condensation:

(2)

3.2. Viscosity measurements

Change in the sol viscosity as well as the transformation of physical appearance of clear sol to transparent gel should establish the formation of 3-D silica frameworks. A plot

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showing the sol viscosity change with respect to time is given in Fig.2 corresponding to different stages of gel formation. The viscosity was observed in four different stages, each has 900 s duration. A constant shear rate of 100 s^{-1} and ambient temperature was maintained during the viscosity monitoring. Initially water glass derived silica sol behaved similar to water and did not show any significant viscosity. At this stage, the sol had a free-flow nature. After 1800 s the sol transformed turbid and exhibited sluggish flow indicating the initiation of gelation. At this stage, viscosity increased significantly reaching a maximum of 870 mPa.s. Further application of mechanical stress, destroyed the gel assembly into tiny gel fragments and once again induced free-flow. At this time, the gel viscosity decreased and maintained a constant rate of ~220 mPa.s. It is found that the condensed water glass silica gel could offer smooth flow when an external mechanical force is applied just after gelation point.
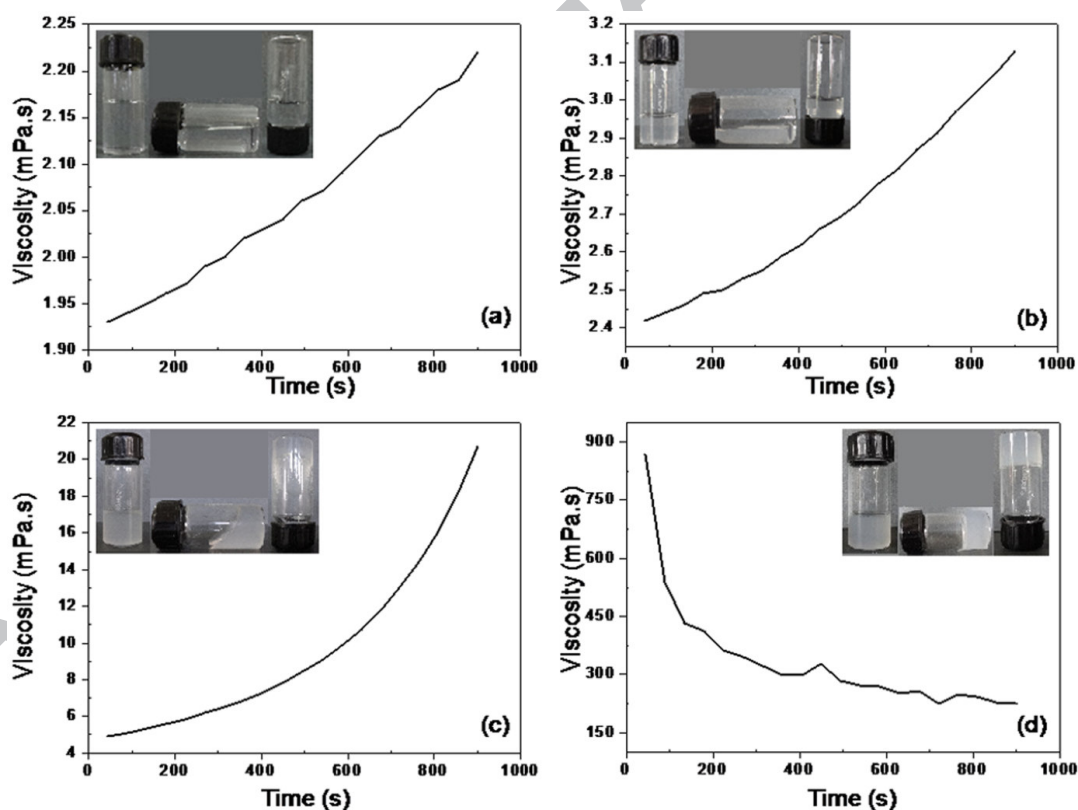

Fig. 2. Viscosity measurement of sol-gel silica.

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The gelation does not affect the pH of the system. The acidic silicagel upon injection into ammonia chemical bath readily formed an assemblage and silica gel granule with good spherical shape could be formed. The injected nano particulate silica gel attained good shape retention indicating that sufficiently strong nano-casting had taken place.

3.3. Surface area and surface characteristics

The gel assembly and its effect on the pore formation nature are confirmed by Field-Emission Scanning Electron Microscopy (FE-SEM). The images of the unmodified and APTMS, PEI modified spherical silica supports just after the solvent exchange and drying are given in Fig.3. The particulate silica gel network is apparently seen in the "as dried" silica gels (Fig.3(a)). Macroporous nature is clearly visible in the SEM image of this sample. Upon amine modification, surface texture gradually transformed to a denser texture and surface-pores decreased considerably due to the distribution of amine molecules on the particle surfaces as well as within the marcopores. In SiO_2 gel supports prepared with 5 wt % PEI, SEM image showed the presence of a reasonable surface porosity (Fig.3b). Surface morphology is very much different when the gel bead was modified with high amount of PEI. The SEM image in Fig.3 corresponds to gel supports modified with 15 wt% PEI. In this sample, the SiO_2 particles are no longer visible as they were completely covered with the amine layer. The support revealed almost flat surface profile at the observed magnification. In case of 2 wt %APTMS modified SiO_2 supports, the SEM image revealed a porous layer with a completely different surface texture on the bead surface. This could be attributed to the high chemical reactivity of APTMS which reacts readily with acidic SiO_2 gel surface and get attached very uniformly even inside the pores and pore walls, indicating its efficiency on surface modification (Fig.3(d)).
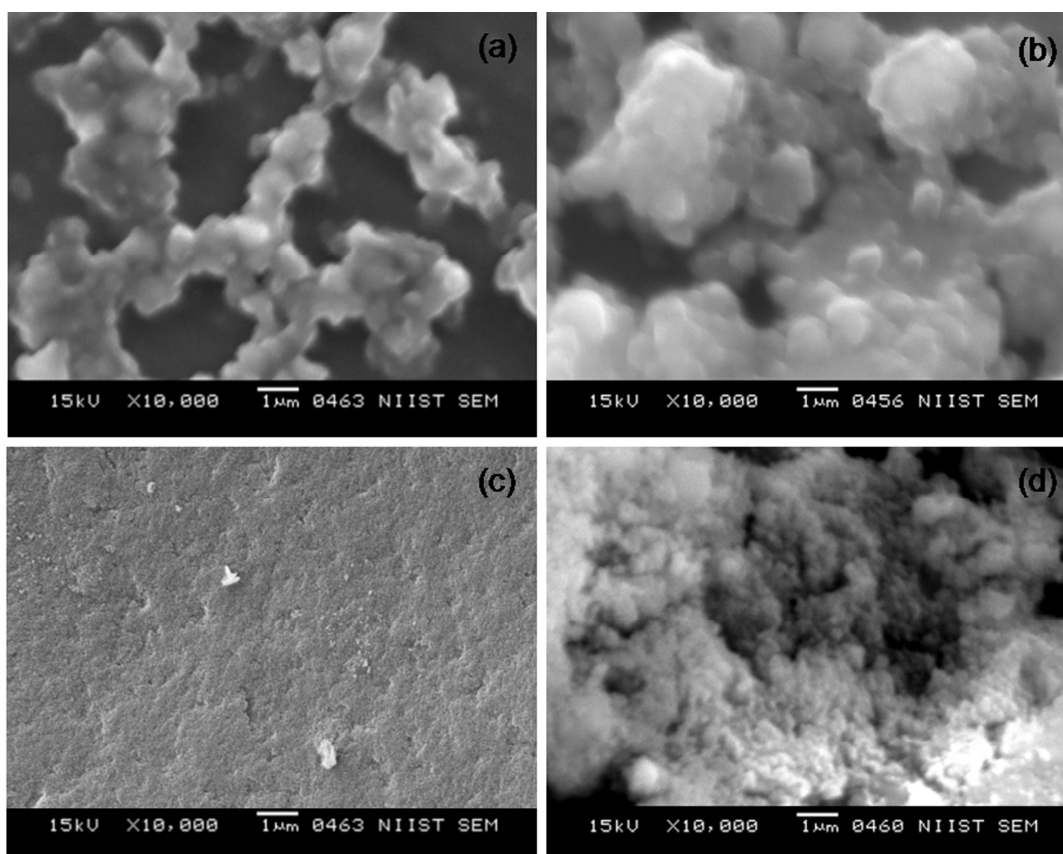
Fig.3. FE-SEM images of silica bead microstructures for (a) unmodified SiO_2; (b) SiO_2-5% PEI; (c) SiO_2-15%PEI and (d) SiO_2-2%APTMS.

The effect of amine uptake and its role on thermal stability is monitored using thermogravimetry (TG) and the weight change curves with respect to modified and unmodified SiO_2 gel supports are shown in Fig.4(a&b). The "as prepared" unmodified silica gel supports showed three major weight loss steps in the TGA curves (Fig.4a). In first stage up to 127 °C a weight change was noticed. It was attributed to the dehydration effect mainly caused by the removal of free water, moisture and solvated molecules occluded in the gel support. The second weight change has occurred up to 480 °C due to dehydroxylation of silanol groups in the bulk gel. In this region, the DTA curve also shows a broad endothermic peak with maximum temperature of 254 °C. The third step observed at temperatures higher than 480 °C should be due to the oxidation of ethyl groups of TEOS used for surface

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modification of the silica beads [26]. The TG analysis confirmed that the gel supports have thermal stability with <12% weight loss. In comparison to unmodified silica gel beads, TG curves corresponding to amine modified supports exhibited increased weight loss with temperature, the amount of which was directly proportional with amine loading (Fig.4b). Silica gels impregnated with PEI showed a weight loss step at around 180 ^{o}C, indicating that dehydroxylation began effectively at this temperature. Below this temperature, a weight loss of only ~4% occurred possibly due to loss of adsorbed H_2O and organic solvents held in gels. Above 180°C, the weight loss could also happen due to PEI decomposition giving its actual amount accepted by the gel supports. Based on the TG weight loss between 180 to 550°C, the amine loading was calculated and presented in Table 1. In PEI modified supports; maximum weight loss was observed for SiO_2-15%PEI samples indicating the high amine content in this case. TG curve corresponding to APTMS modified samples showed lower weight loss compared to PEI containing sample, as in this case only 2% APTMS was used. Moreover, this sample had dehydroxylation point at a much higher temperature, around 300 ^{o}C, indicating its thermal stability advantage compared to PEI. TG analysis confirmed that the water glass derived silica gel beads acted as good matrix for effective loading of amine containing molecules.
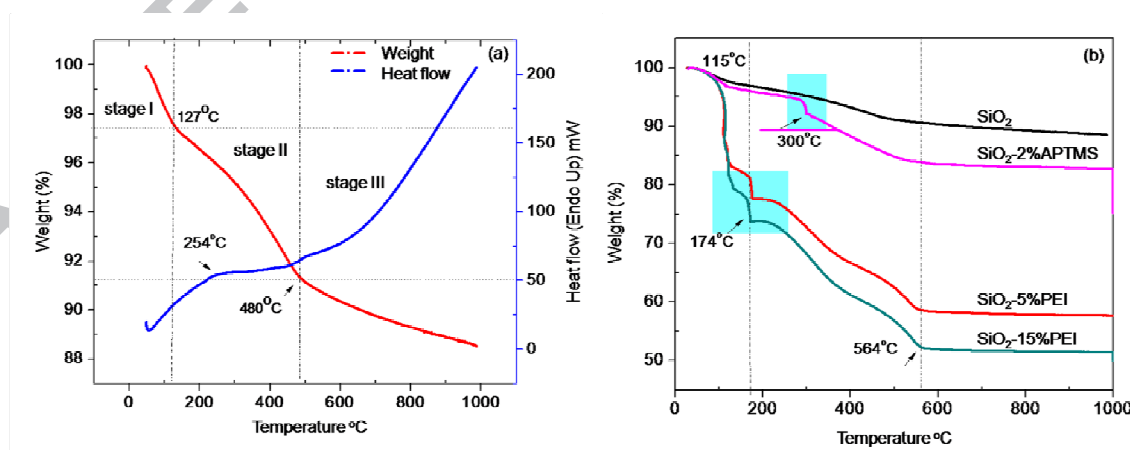

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Fig.4. (a) TG-DTA curve for unmodified silica and (b) TGA plot for amine modified silica samples.

Type of amine, its extent of loading and its interaction with the surface functional groups such as acidic and hydroxyl moieties play decisive role in the structure-assembly and pore evolution during casting. Pore characteristics of silica gel beads as examined using N_2 adsorption-desorption isotherms are given in Fig.5. As expected, all samples show Type –IV isotherms which are typical to mesoporous materials. The pore volume (corresponding to P/P_o value of 0.85) and surface area values derived from N_2 adsorption are also summarized in Table 1. It is shown that the water glass derived silica gel under given synthesis conditions resulted in the surface area of 304.7 m^2 g^{-1}, which decreased notably when amine modification was made. Isotherms also showed differences in hysterisis depending upon the amine modification indicating pore structural changes. PEI impregnated silica gel supports showed comparatively smaller hysterisis which decreased with increasing PEI content. It is possible that the PEI uptake formed a dense surface layer over porous silica matrix as also seen in SEM analysis. A decrease in total pore volume was observed in these samples. Interestingly, APTMS modification did not affect the surface area (283.46 m^2 g^{-1}) or total pore volume (0.449 cm^3 g^{-1}) values of the samples critically. These results are in line with SEM observations (Fig.3(d)), where the macrostructure of the modified silica was found coated uniformly with APTMS. The porosity features and pore volume measurement results were found consistent with the SEM results as well as amine loading values measured by TGA studies (Table 1). In comparison with PEI, surface modification using APTMS could be advantageous because PEI seems to have formed a coating that blocked at least some of the pores. However, as the PEI loading in the samples were higher than APTMS, further studies are required for a complete understanding of the influence of amine molecular structure on pore structure formation of the adsorbent beads.
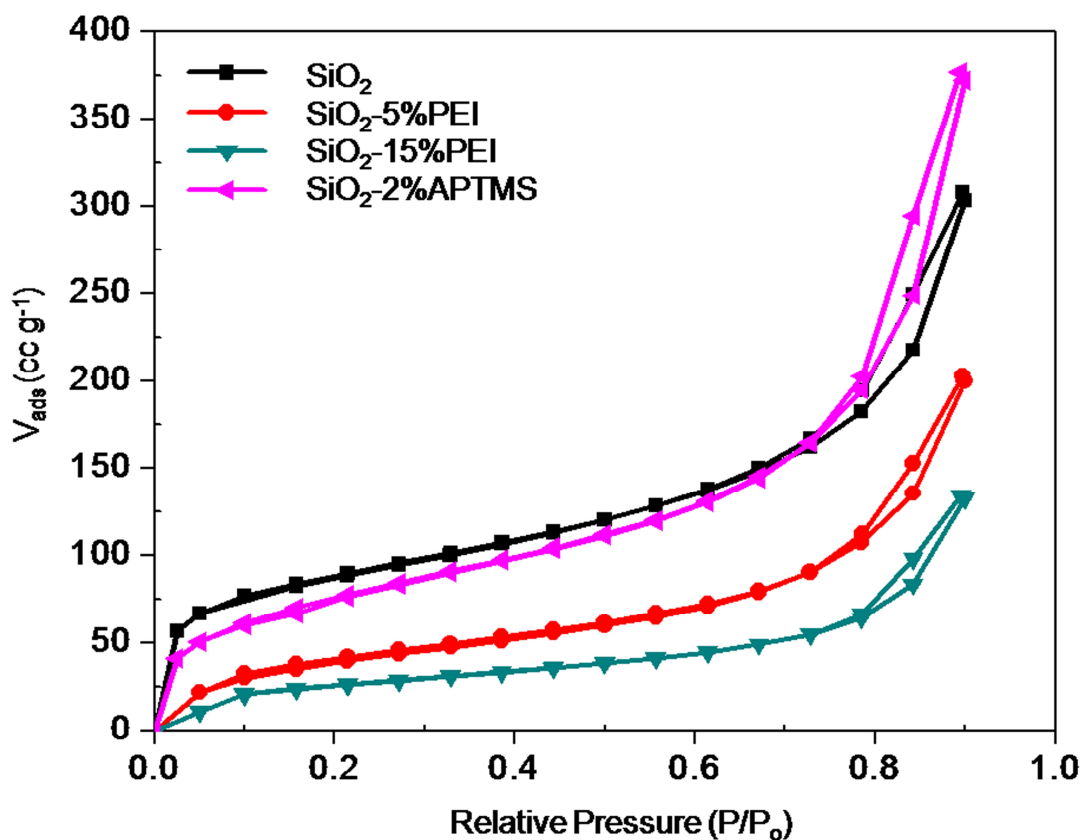
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Fig. 5. N_2 adsorption-desorption isotherms for unmodified and modified silica microspheres.

Table 1

Amine loading and pore structural properties of the modified water-glass beads

Samples prepared in this work	Surface Area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Amine loading (%)
SiO_2	304.71	0.3827	--
SiO_2- 5% PEI	148.78	0.2357	16.06
SiO_2- 15% PEI	96.33	0.1526	20.00
SiO_2- 2% APTMS	283.46	0.4490	12.50

3.4. CO$_2$ adsorption studies

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For CO_2 adsorption in the absence of moisture, the main possibility of bonding is hydrogen bonding formed between H group of amine and the O group of polar C=O bond that is relatively weak compared with adsorption in presence of moisture which enables the relative ease of regeneration of the adsorbent under dry conditions [28].

FT-IR spectra of modified and unmodified silica gel beads before and after CO_2 adsorption are shown in Fig.6. The wide peak with strong intensity at 1100 cm^{-1} and the weak peak near 800 cm^{-1} were assigned to the asymmetric and symmetric bending of Si-O-Si bonds. The peak near 472 cm^{-1} is due to the bending of O-Si-O bonds. In the spectra of unmodified silica gel, the wide band at 3426 cm^{-1} and the peaks at 1640 and 944 cm^{-1} correspond to the hydroxyl groups adsorbed on the surface as well as the stretching of Si-OH bonds respectively [29]. For amine modified samples the peak around 1600 cm^{-1} corresponds to the introduction of –NH- containing APTMS and PEI [30]. With the percentage increase in PEI content the –NH- peak area also increases and its minimum for APTMS loaded aerogel. After adsorption, the peaks that appeared in all the spent samples at 1749 and around 2340 cm^{-1} is due to the adsorption of CO_2 [5, 30].
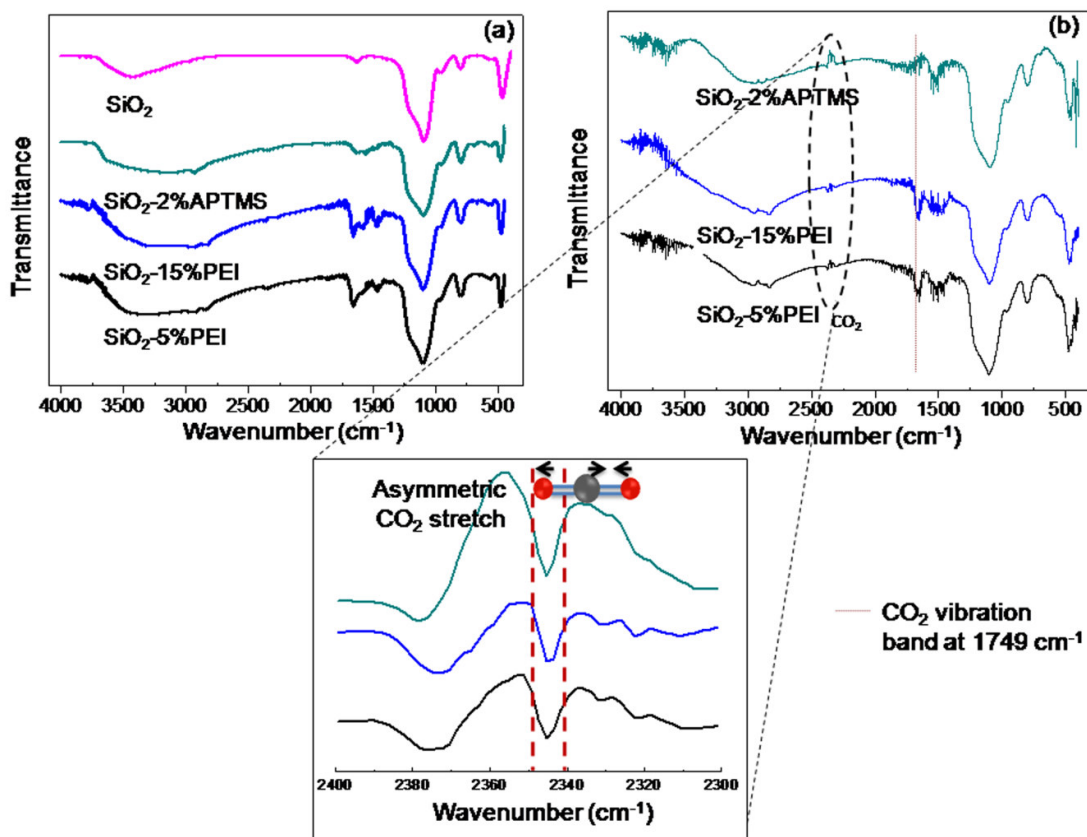
Fig. 6. FTIR spectra of pure and amine loaded microspheres before adsorption (a) and after adsorption (b).

CO_2 adsorption results measured using TGA is listed in Table 2. In this method, we have initially cleaned the adsorbent at 130 ^{o}C in flowing N_2. The temperature was then decreased to 50 ^{o}C and gas was switched to CO_2. The weight gain with time was monitored and based on that the adsorption capacity and rate of adsorption were calculated. Desorption was carried under flowing N_2 at 130 ^{o}C. Fig.7(a) shows the gravimetric adsorption curves for amine loaded samples. From the data shown in Fig.7 and Table 2, it is evident that the adsorption capacity increases with amine loadings resulting in a linear trend of adsorption capacity with amine contents. SiO_2-2%APTMS supports showed CO_2 uptake of 0.67 mmol g^{-1}. Similarly, an adsorption capacity of 0.88 mmol g^{-1} was observed for SiO_2-5%PEI and 1.16

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mmol g^{-1} was measured for SiO_2-15%PEI sample. The adsorption rate after 3 minutes for SiO_2-15%PEI sample (Fig.7(b)) at 50 ^{o}C was about 0.269 mmol g^{-1} min^{-1}.

Fig.8 summarizes the changes in characteristics of water glass derived silica gel solids such as its surface area, pore volume and CO_2 adsorption capacity along with change in amine content.
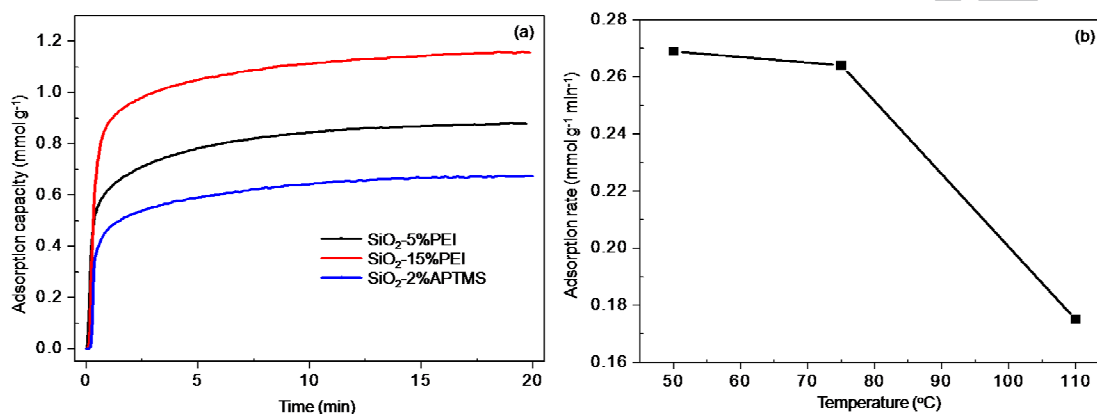

Fig. 7. Effect of amine modified water glass gel sorbents on CO_2 adsorption: Gravimetric adsorption curves for amine modified samples (a); Adsorption rate of SiO_2-15%PEI at different temperatures after 3 minutes (b).

Table 2

CO_2 adsorption capacities of the modified water-glass beads

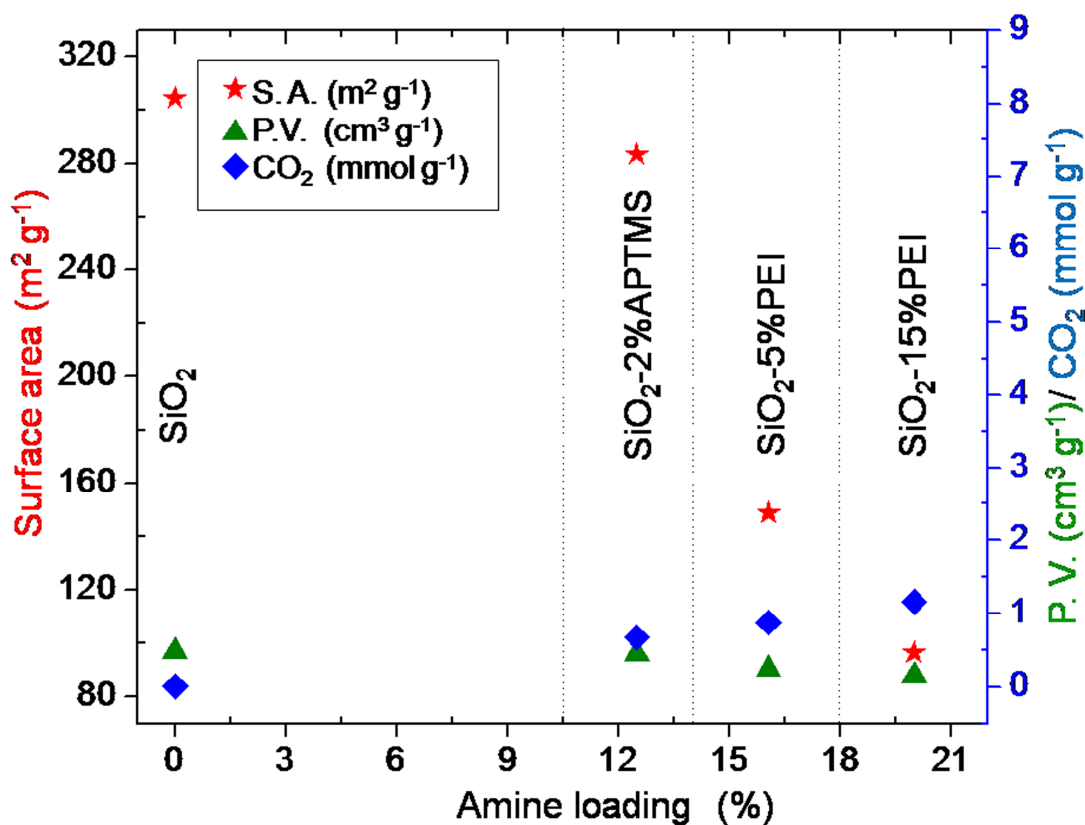| Solid Adsorbent	CO_2 adsorption capacity (mmol g^{-1})	Adsorption rate after 3min. (mmol g^{-1} min^{-1})
SiO_2	0.21	0.064
SiO_2- 5% PEI	0.88	0.243
SiO_2- 15% PEI	1.16	0.269
SiO_2- 2% APTMS	0.67	0.184

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Fig. 8. Surface properties and CO_2 adsorption as a function of amine loading.

The volumetric adsorption capacity of gel supports at 1 bar for SiO_2 and SiO_2-15%PEI are plotted against temperature and presented in Fig.9. The adsorption values measured by the volumetric method were slightly lower than the values measured by the gravimetric method (Fig. 7a) for the SiO_2-15%PEI samples. The low adsorption rate of CO_2 in the sample could be the reason for the lower adsorption values measured here. It is possible that the volumetric measurement program we have employed, was inadequate for realising full adsorption (and desorption) of CO_2. In the gravimetric measurement protocol samples had been kept for 20 minutes and equilibrium adsorption could be verified from the plot. Even with this slightly anomaly in measurement, the volumetric adsorption study helped us to realize that the silica gels without any amine functionality showed decrease in its adsorption performance with increasing temperatures. Interestingly, amine modified gel

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sorbent retained a significant part of the adsorption capacity even at a high temperature of 100°C.
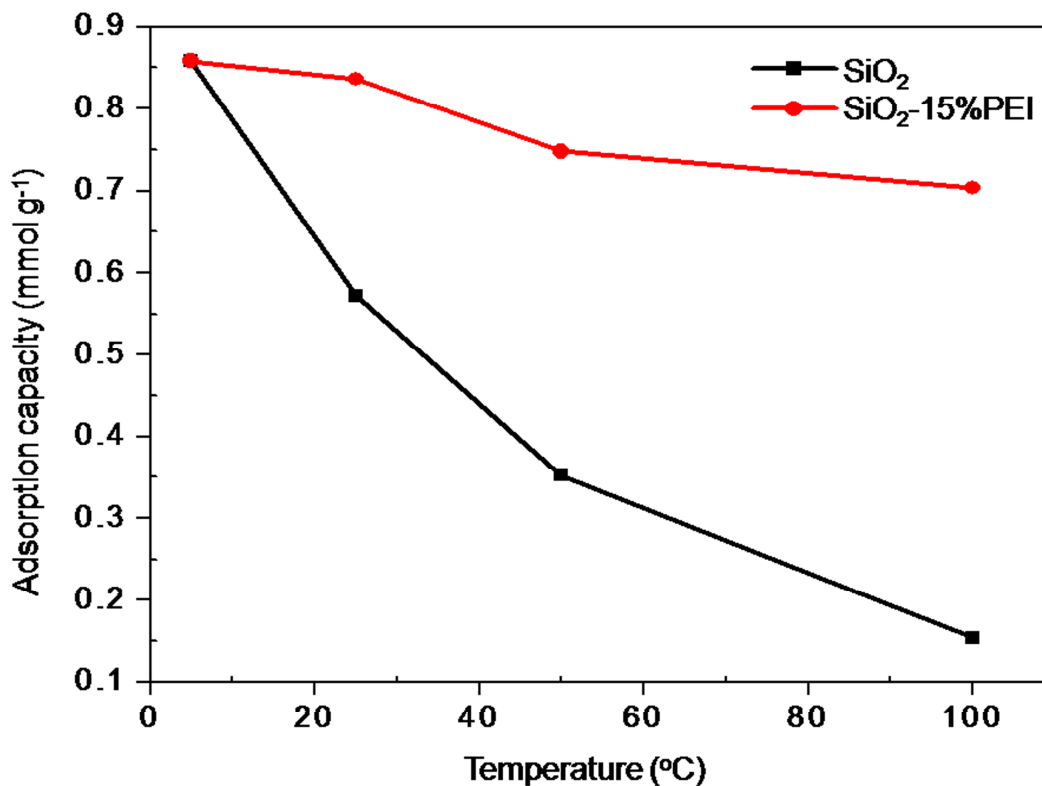

Fig. 9. Adsorption capacity at different temperatures for SiO_2 and SiO_2-15%PEI (Data measured volumetrically).

4. Conclusion

This study addressed the highly relevant issue of the design of industrially viable cost effective solid-sorbents for CO_2 sorption. A porous silica gel-solid in the form of mechanically stable spherical bead was designed using low-cost, easily available water-glass precursors via a sol gel approach. The use of water-glass precursors resulted in the formation of highly stable, particulate sol which underwent conversion from free-flow to injectable gels upon aging. This enabled us to fabricate spherical gel granules containing abundant surface

hydroxyl groups, thus facilitating further chemical modifications. Thus formed gel solid was chemically modified with two kinds of amines, PEI and APTMS respectively, in order to make them selective for CO_2 capturing. The gel supports retained hydrophilic functional groups up to 127 ^{o}C which was important to have low temperature CO_2 adsorption. A surface area of 304.7 m^2 g^{-1} was obtained for water glass derived silica gel support. The amine modification considerably decreased the bulk surface area when amine loading was high. The gel support was found suitable for amine uptake resulting in enhanced CO_2 adsorption. Silica supports modified with 15 wt % PEI showed adsorption capacity value 1.16 mmol g^{-1} at 50 ^{o}C. Amine modified silica supports showed enhanced thermal stability and retained significant CO_2 adsorption values even at an adsorption temperature of 100 ^{o}C.

Acknowledgements

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List of Figure and Table captions

Fig.1.(a) Zeta potential and (b) size distribution curve for silica sol prepared at pH 4.

Fig.2. Viscosity measurement of sol-gel silica.

Fig.3.FE-SEM images of silica bead microstructures for (a) unmodified SiO_2; (b) SiO_2-5% PEI; (c) SiO_2-15%PEI and (d) SiO_2-2%APTMS

Fig.4.(a) TG-DTA curve for unmodified silica and (b) TGA plot for amine modified silica samples.

Fig.5.N_2 adsorption-desorption isotherms for unmodified and modified silica microspheres

Fig.6.FTIR spectra of pure and amine loaded microspheres before adsorption (a) and after adsorption (b)

Fig.7. Effect of amine modified water glass gel sorbents on CO_2 adsorption: Gravimetric adsorption curves for amine modified samples (a); Adsorption rate of SiO_2-15%PEI at different temperatures after 3 minutes (b).

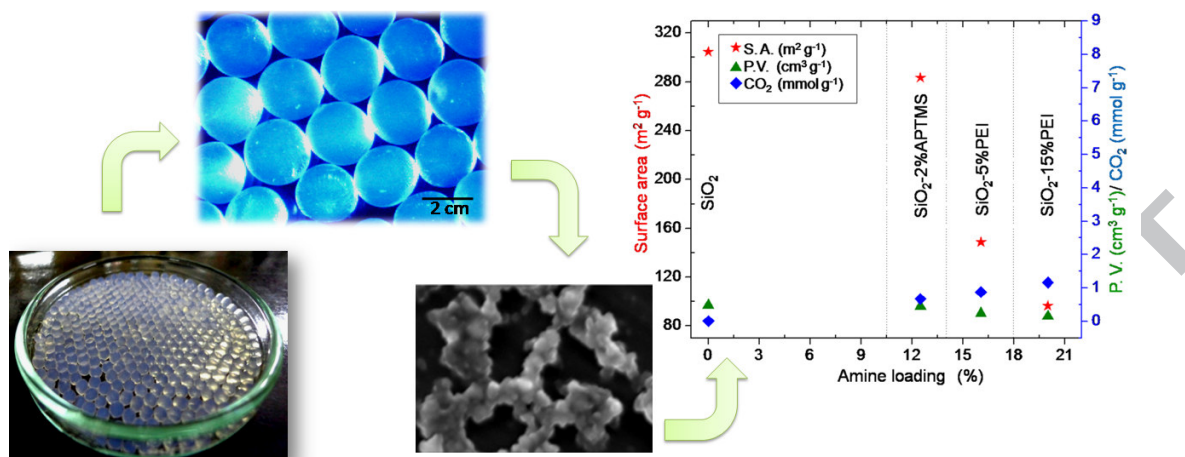**Fig.8.**Surface properties and CO_2 adsorption as a function of amine loading.

Fig.9. Adsorption capacity at different temperatures for SiO_2 and SiO_2-15%PEI (Data measured volumetrically).

Table captions

Table 1

Amine loading and pore structural properties of the modified water-glass beads

Table 2

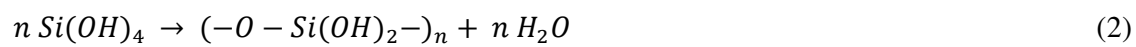CO_2 adsorption capacities of the modified water-glass beads

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Highlights

- Solid silica gel beads made from low cost sodium silicate precursor.

- Linear trend in CO_2 adsorption with increased amine loadings.

- Significant CO_2 adsorption at lower temperature.

- Effect of surface area, pore volume, CO_2 adsorption w. r. t. amine loading studied.

Condensation:

$$n\,Si(OH)_4 \rightarrow (-O - Si(OH)_2-)_n + n\,H_2O \tag{2}$$

Silica gel