Chapter 4: A diamino-functionalized silsesquioxane pillared graphene oxide for CO₂ capture

In the race for viable solutions that could slow down carbon emissions and help in meeting the climate change targets a lot of effort is being made towards the development of suitable CO₂ adsorbents with high surface area, tuneable pore size and surface functionalities that could enhance selective adsorption. In the study reported in this chapter, we explored the use of silsesquioxane pillared graphene oxide for CO₂ capture; we modified silsesquioxane loading and processing parameters in order to obtain pillared structures with nanopores of the tailored size and surface properties to maximize the CO₂ sorption capacity. Powder X-ray diffraction, X-ray photoelectron and Fourier transform infrared spectroscopies, thermogravimetric analysis, surface area measurements and CO₂ adsorption measurements were employed to characterize the materials and evaluate their performance. Through this optimisation process, materials with good CO₂ storage capacities of up to 1.7/1.5 mmol/g at 273 K/298 K in atmospheric pressure, were achieved.

Published as:

4.1. Introduction

The level of atmospheric carbon dioxide emissions, one of the main contributors to global warming, has been increasing dramatically year after year, and despite the attempts towards the moderation and decrease of greenhouse gas production the situation seems irreversible. CO₂ is mainly generated from fossil fuel combustion and since there will be no substitute main energy source in the immediate future, the most promising plan of action is Carbon Capture, Utilization and Storage (CCUS).¹

The capture process of CCUS is focused mainly on industries with high CO₂ emissions, such as power plants, refineries and oil production, while Enhanced Oil Recovery (EOR), although not of universal application, offers a unique financial incentive for capturing carbon: using waste CO₂ as a source material for producing hydrocarbons and at the same time preventing its harmful release into the atmosphere. In EOR CO₂ is injected in almost depleted oil fields in order to force out residual oil and natural gas. The problematic amine-based and ammonia solutions that have been broadly used until now for CO₂ capture, need to be replaced by sorbents that are low-cost, easy to scale up and that can be regenerated and reused at low energy cost.²³ It is well-known that carbon materials such as amorphous carbon, nanotubes, fibers and graphite can be used as sorbents/sieves,⁴⁻⁹ catalytic substrates,¹⁰ membranes,¹¹ etc. due to their low mass in combination with chemical inertness, thermal stability and mechanical properties.

Theoretically, defect-free isolated graphene sheets have a very high surface area (2630 m²/g),¹² in addition to being easily (chemically) modified and exhibiting superior mechanical and thermal stability. Graphene is also chemically inert and thus represents an ideal system for sorption and catalysis applications. If the full scientific and technological potential of graphene is to be achieved, lightweight, open 3D structures with high surface area, tuneable pore size and aromatic functionalities must be synthesized. However, the direct use of the unique surface properties of isolated graphene sheets is hampered by the underlying physical–chemical constraints, since due to their aromatic π-systems these structures are extremely prone to aggregation. It is thus clear that the only way to develop nanostructured materials based on graphene or its derivatives as building blocks, is to devise means to maintain the sheets
A diamino-functionalized silsesquioxane pillared GO for CO$_2$ capture

detached. This can be implemented by taking advantage of the concept of intercalation chemistry and the so-called pillaring method, which involves the insertion of suitable and robust organic and/or inorganic species as pillars between the layers. These methods have been successfully applied in other layered structures such as clays$^{13}$ and layered double hydroxides.$^{14}$ Pillaring of graphene sheets can provide the necessary structural stability and keep the single carbon layers at a controlled distance, so that a maximum active surface area is easily accessible to small molecules. In such a way, new micro- and meso-porous materials with larger pore sizes than traditional porous materials such as zeolites can be designed. In 2008, using a multiscale theoretical approach Dimitrakakis et al.$^{15}$ proposed a 3D nanostructure consisting of parallel graphene layers, connected by carbon nanotube (CNT) pillars. This system, consisting mainly of sp$^2$ hybridized carbon, shows superior structural stability, tuneable porosity and improved storage properties. CNT pillared graphene combines high surface area, narrow and tuneable pore size distributions with available aromatic functionalities arising from both the graphene layers and the CNTs. It is exactly this combination, which makes this class of materials most suitable candidates for the “Holy Grail” storage adsorbent for important gases such as H$_2$. Various organic and/or inorganic pillars between graphene layers can impart enhanced and/or diverse properties for gas separation or catalysis, while further “functionalization” can be carried out by the well-established carbon chemistry. Furthermore, by properly choosing the pillaring species, 3D porous structures can be conceived, which are superior to metal organic frameworks (MOFs)$^{17}$ in terms of stability at higher pressure and durability in normal environmental conditions.

A particularly promising approach is the intercalation of cubic silsesquioxanes as pillaring species in chemically oxidized graphene (graphene oxide, GO). Cubic siloxanes (silsesquioxanes) are synthesized from the hydrolytic condensation of the corresponding trifunctional organosilicon monomers, and offer the opportunity to realize materials with extremely well-defined dimensions and behaviour.$^{18,19}$ Cubic siloxanes of the type $X_8Si_8O_{12}$, where $X$ can be -(CH$_3$)$_3$NH$_2$, or -(CH$_3$)$_3$NH(CH$_2$)$_2$NH$_2$, have been successfully employed as precursor reagents for pillaring inorganic layered solids such as clays$^{20-24}$ or metal(IV)-H- phosphates.$^{25}$
In the study reported here we focused on the synthesis and characterization of novel pillared materials where amino-functionalized cubic silsesquioxanes were intercalated among GO layers at different loadings. Silsesquioxanes assure the robustness of the 3-D network of adjacent graphene sheets, while the unreacted amine groups in the open space between the GO sheets warrant strong CO₂ adsorption.

4.2. Experimental Section

4.2.1. Materials

Graphite (purum, powder <0.1 mm) and N-[3-(trimethoxysilyl) propyl]-ethylenediamine (EDAPTEOS, 97%) were purchased from Sigma Aldrich, whereas potassium chlorate (KClO₃, 99+%) was acquired from Alfa Aesar, sulfuric acid (H₂SO₄, 96 %) and ethanol (absolute for analysis) from Merck, and nitric acid (HNO₃, 65 %) from Penta Chemicals Unlimited, and sodium hydroxide carbonate (NaHCO₃, >99.7 %) from Riedel-de Haën. All reagents were of analytical grade and used without further purification. The water used in the experiments was distilled and deionized.

4.2.2. Graphene Oxide Synthesis

GO was produced through graphite powder oxidation using a modified Staudenmaier's method²⁶,²⁷ that leads to a higher amount of epoxy groups compared to carboxy and hydroxy groups, and thereby a starting material that favours reactions with amine ending moieties.²⁸ In a typical synthesis, 10 g of powdered graphite were added to a mixture of concentrated sulfuric acid (400 mL) and nitric acid (200 mL), while stirring and cooling in an ice-water bath in order to absorb the heat released during the very exothermic chemical reaction. Potassium chlorate powder (200 g) was added to the mixture in small portions, while stirring and cooling. The reaction was quenched after 18 h by pouring the mixture into distilled water and the oxidation product was washed until an almost neutral (~6) pH value was reached. The sample was then dried at room temperature by air-drying, where the sample was spread onto a glass plate and left to dry, as well as by freeze-drying (a laboratory freeze dryer BK-FD10 series by Biobase was used), where the sample was redispersed in 150 mL of H₂O, frozen by contact with liquid nitrogen and the ice was subsequently removed by sublimation at low pressure.
4.2.3. Formation of the pillaring agent

The organosilane used in this study was N-[3-(trimethoxysilyl)propyl]-ethylenediamine (EDAPTEOS). The formation of the octameric oligosiloxanes (see Figure 4.1) from the hydrolytic polycondensation of the monomer occurs after dilution of EDAPTEOS in ethanol–water (v/v = 14/1) to give a solution of 0.45 M concentration.22-25, 29

4.2.4. Preparation of silsesquioxane pillared graphene oxide

A sample of 200 mg of GO was dispersed in 100 mL water by stirring for 24 h. The pH value of the dispersion was adjusted to slightly basic (~7.1) by adding a few drops of 0.1 M NaHCO₃ solution so that amines (~NH₂) are not protonated and thus easily form covalent bonds. Subsequently, aliquots of the siloxane solution were added such that 1.5, 4.5 and 9 mmol loadings were achieved. Upon addition of the siloxane solution the GO solid swelled instantly and flocculation was noticed (see Figure 4.2(a)). After stirring for 24 h, the GO-organosilane aggregates were washed with water two times, separated by centrifugation and either air-dried (see Figure 4.2(b)), and freeze-dried (see Figure 4.2(c)) as described above. The samples are denoted PILGD₅AD and PILGD₅FD (where x is the loading).

![Figure 4.1. The cage-like structure of the siloxane](image)
4.3. Results and Discussion

Oxidizing graphite powder following the modified Staudenmaier's method,\textsuperscript{26} produces exfoliated hydrophilic single layer flakes of graphene oxide (GO), which are perfectly dispersed in water. As detailed above, the pillaring solution was derived from controlled hydrolysis of N-[3-(trimethoxysilyl) propyl]-ethylenediamine (EDAPTEOS) and hydrolytic condensation of the silanes takes place smoothly in an ethanol–H\textsubscript{2}O solution, resulting in the creation of an octameric cubic structure.\textsuperscript{23,25} The immediate flocculation observed when the ethanolic solution containing the pillaring agent was added to the GO suspension, hints to the insertion of cubic siloxanes between the GO layers through covalent bonding via the amide functionality of the organosilane molecules. Interaction of the primary aliphatic amines of the EDAPTEOS end groups with GO is expected to take place mainly via nucleophilic substitution reactions on the epoxy groups of GO.\textsuperscript{27,30}

The X-ray diffraction (XRD) patterns of the pristine graphite, GO and the PILGD samples are shown in Figure 4.3. Note that the sharp peak at 21.4° visible in most of the samples, originates from the silicon oxide used as a
A diamino-functionalized silsesquioxane pillared GO for CO$_2$ capture

substrate for the measurements. The pattern of pure graphite exhibits a peak at 26.6$^\circ$ corresponding to the basal spacing $d_{002} = 3.34$ Å, while for graphene oxide a 001 reflection$^{30, 31}$ appears at 11.9$^\circ$, consistent with a basal spacing of $d_{001} = 7.4$ Å. Treatment of GO with the siloxane cubes leads to a shift of the peak to lower angles, which confirms an expansion of the interlayer space by the organofunctionalized silicon oxide cubes inserted as bonded pillars between GO sheets. In the case of the air-dried samples, two peaks are distinguished in the XRD patterns, one in the range of 6.3–7.7$^\circ$ and a second one at 9.6$^\circ$. The existence of these two peaks is due to the different orientations of the cubes, facilitated by the flexibility of the aliphatic chains.$^{32}$ Applying the Bragg formula ($n\lambda = 2d \sin \theta$), and bearing in mind that the thickness of a graphene oxide layer is 6.1 Å,$^{33}$ the interlayer distances giving rise to the two peaks are calculated to amount to 11.4, 14 and 9.2 Å, respectively. Taking into account the intercalant's size as marked in Figure 4.1, one concludes that it has adopted a very slightly inclined orientation between the GO sheets. There is also a very broad feature centred around the peak position of pure GO, which indicates that not all layers are pillared and very small coherently diffraction domains of unfilled GO persist in between the pillared structure. On the other hand, in the case of the freeze-dried samples the peak positions cannot readily be discerned because the diffraction pattern shows very broad features, pointing to small coherently diffracting domains.

Thermogravimetric analysis (TGA) was performed on the air-dried silsesquioxane-pillared structures in order to determine the relative amount of silicon oxide for each loading; the results are presented in Figure 4.4. Heating up to 250 $^\circ$C an initial mass loss of $\sim$24 % is noticed, which is attributed to the removal of the adsorbed water and of the oxygen containing groups of the GO.$^{30}$ Increasing the temperature to 350 $^\circ$C, a second mass loss of $\sim$12 % is recorded, which can be assigned to the removal of the organic groups bonded to the siloxane cubes, and successively a third weight loss of approximately 45 % indicates combustion of the graphene layers. From the remaining weight after heating to 850 $^\circ$C, we calculated that the inorganic silicon oxide cubes correspond approximately to 10.8, 13.1 and 14.2 % of the total mass of the pillared material obtained with 1.5, 4.5 and 9 mmol loading respectively.
Figure 4.3. XRD patterns of pristine graphite, graphene oxide, and silsesquioxane-pillared graphene oxide prepared with different loadings and either air-dried or freeze-dried.

Figure 4.4. Thermogravimetric analysis curves of the three air-dried silsesquioxane-pillared graphene oxide structures.
Note that the silicon oxide cubes' content does not scale with the loading because in the last step of the synthesis the samples were washed two times to remove the excess amount of cubes as well as the loosely bonded ones.

An additional characterisation tool, which can confirm the successful insertion of the silsesquioxane cubes between GO sheets, is Fourier transform infrared (FTIR) spectroscopy. As shown in Figure 4.5, while pure graphite is an IR inactive solid, graphene oxide exhibits all the IR features expected after oxidation, namely at 3411 cm\(^{-1}\) the hydroxyl stretching vibrations of the C–OH groups, at 1630 cm\(^{-1}\) the C=O stretching vibrations of the –COOH groups, at 1069 cm\(^{-1}\) the C–O stretching vibrations, at 1294 cm\(^{-1}\) the asymmetric stretching of C–O–C bridges in epoxy groups, and at 1646 cm\(^{-1}\) the C=C stretching vibrations of the aromatic ring.\(^{34,35}\) In the case of the pillared samples, extra peaks appear in the spectrum, which are attributed to the presence of the silsesquioxane cubes. In fact, the band at 773 cm\(^{-1}\) is assigned to the stretching vibrations of O–Si–O bonds, and the ones at 445, 596, 1067 and 1197 cm\(^{-1}\) are due to the Si–O–Si bending and stretching vibrations;\(^{32,36}\) together these spectral features confirm the integrity of the silsesquioxane cubes.

![Figure 4.5. FTIR spectra of graphite, graphene oxide (GO) and of the air-dried silsesquioxane-pillared graphene oxide structure PILG\(_{4,5}\)AD](image-url)
The band at 692 cm\(^{-1}\) is due to the C–H bending vibrations of the aliphatic chains of the silsequioxane cubes\(^{32}\) and the one at 920 cm\(^{-1}\) stems from Si–O stretching vibrations.\(^{37}\) The spectral fingerprints of C–N at 1315 cm\(^{-1}\), the asymmetric N\(^+\)-CH\(_3\) deformations\(^{22}\) at 1474 cm\(^{-1}\), the –NH\(_3^+\) deformation\(^{23, 37}\) at 1570 cm\(^{-1}\) and the NH\(_2\) deformation at 1627 cm\(^{-1}\) together testify to the integrity of the aliphatic chains of the cubes.\(^{23}\) Finally, asymmetric and symmetric stretching vibrations of –CH\(_2–\) groups observed at 2931 and 2874 cm\(^{-1}\) reveal the presence of organosilane molecules in the solid. Analogous spectra were obtained for all the other pillared samples (data not shown here).

X-ray photoelectron spectroscopy (XPS) was performed on the three air-dried silsesquioxane-pillared structures in order to verify the presence and integrity of the siloxane cubes in the interlayer space of GO and also to evaluate the quality of the graphene-based material in terms of chemical moieties present after intercalation. The detailed spectra of the C1s and N1s core level regions are shown in Figure 4.6.

Deconvolution of the C1s spectrum requires five components. The first and most prominent peak at a binding energy (BE) of ~284.2 eV is attributed to C–C/C=C bonds within the graphene oxide layers and contributes with respectively 41.4, 38.8 and 48.7\% of the total C1s spectral intensity for PILGD\(_{1.5}\)AD, PILGD\(_{4.5}\)AD and PILGD\(_{9}\)AD. The second one at a BE of ~285.4 eV is due to the C–O bonds of the GO lattice as well as from the C–N bonds of the cubes and makes up 24.7, 24.4 and 31.3 \% of the C1s spectral intensity for the 3 loadings respectively, while the third component at a BE of ~286.9 eV originates from the epoxy groups and its lower intensity with respect to pure GO for all 3 loadings (17.7, 17.0 and 11.3 \% of the total C1s spectral intensity) indicates the formation of covalent bonds.
A diamino-functionalized silsesquioxane pillared GO for CO$_2$ capture

**Figure 4.6.** XPS spectra of the C1s (left panels) and N1s (right panels) core level regions of the silsesquioxane-pillared GO structures obtained with the three different loadings.
Table 4.1. Stoichiometry of the air-dried silsesquioxane-pillared GO structures as deduced from the XPS analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>PILGD$_{1.5}$AD</th>
<th>PILGD$_{4.5}$AD</th>
<th>PILGD$_{9}$AD</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>78.8</td>
<td>63.9</td>
<td>66.9</td>
</tr>
<tr>
<td>O</td>
<td>10.8</td>
<td>21.7</td>
<td>21.7</td>
</tr>
<tr>
<td>N</td>
<td>3.5</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Si</td>
<td>6.9</td>
<td>10.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Finally, the two components at BEs of ~288.2 and ~289.8 eV are attributed respectively to C=O bonds (relative intensity 12.3, 12.9 and 5.8 % for the three loadings) and to carboxylic groups present in the graphene oxide sheets (relative spectral intensities 3.9, 6.9 and 2.9 % for the three loadings).

Through the analysis of the XPS spectra of the N1s core level region additional insight on the type of interactions can be gained. The nitrogen spectrum requires three components for a good fit: the first one at a BE of ~398.4 eV is attributed to the covalent bonds formed between the amines and the epoxy groups (relative spectral intensities 25.7, 22 and 33.8 % for the three loadings); the second contribution at ~400 eV is due to amines of the precursor and amounts to respectively 50.7, 56.7 and 44.8 % of the total N1s intensity and the last one at a BE ~401.4 eV stems from protonated amines (relative spectral intensities 23.6, 21.3 and 21.4 % for the three loadings).

The atomic percentages of the elements present in the samples were calculated and are presented in Table 4.1. The silicon content agrees with the data of the thermal analysis of the samples.

The porous structure of the different silsesquioxane-pillared GO samples and of pure GO was studied by recording the N$_2$ adsorption–desorption isotherms at 77 K; the data are presented in Figure 4.7. The BET specific surface area, deduced from the adsorption data and reported in Table 4.2 for all samples, is significantly higher for the freeze-dried samples. In fact, for the latter it reaches more than 5 times larger values than those of the air-dried ones synthesized with the same silsesquioxane loading.
A diamino-functionalized silsesquioxane pillared GO for CO\textsubscript{2} capture
Figure 4.7. $N_2$ adsorption (full symbols)-desorption (empty symbols) isotherms at 77 K for graphene oxide (air dried and freeze-dried) and for all silsesquioxane-pillared GO structures prepared with different loadings and both ways of drying.

Table 4.2. The values of the specific surface area of GO and silsesquioxane-pillared GO as deduced from $N_2$ adsorption measurements at 77 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>AD</th>
<th>FD</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>PILGD$_{1,5}$</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>PILGD$_{4,5}$</td>
<td>9</td>
<td>46</td>
</tr>
<tr>
<td>PILGD$_9$</td>
<td>8</td>
<td>42</td>
</tr>
</tbody>
</table>

The pillared structures were examined with SEM in order to spot the differences in the structures for the two different ways of drying; representative images of the PILGD$_{4,5}$AD and PILGD$_{4,5}$FD samples are shown in Figure 4.8. As expected, by simply air drying the samples in ambient conditions, we get compact stacks of graphene oxide layers since with the removal of water the structure shrinks and the layers are only kept apart by the silsesquioxane cubes (left image of Figure 4.7). On the other hand, when freeze-drying is employed, the ice crystals sublime, leaving behind pores in the structure. In the SEM image (Figure 4.8, right picture) one easily discerns a more foam-like macroscopic structure of the sample, very distinct from the one resulting from air-drying. This explains the increased specific surface area for the freeze-dried samples.
The CO$_2$ adsorption behaviour for all samples was investigated by recording the corresponding adsorption isotherms at 273 K and 298 K, up to 1 bar (see Figure 4.9).

![Figure 4.8. Representative scanning electron microscopy images of the air-dried (PILGD$_{4.5}$AD, left) and freeze-dried (PILGD$_{4.5}$FD, right) silsesquioxane-pillared GO structures. The scalebar corresponds to 1 μm](image-url)
Figure 4.9. CO$_2$ adsorption (full symbols)-desorption (empty symbols) isotherms at 273 K and 298 K up to 1 bar for graphene oxide (air dried and freeze-dried) and for all silsesquioxane-pillared GO structures prepared with different loadings and both ways of drying.
For the neat GO samples, although the uptake is relatively poor, the freeze-dried GO is able to capture twice as much CO$_2$ [16.1 cm$^3$/g (0.72 mmol/g) and 15.3 cm$^3$/g (0.68 mmol/g), at 273 K and 298 K respectively] as the air-dried one [8 cm$^3$/g (0.36 mmol/g) and 7.7 cm$^3$/g (0.34 mmol/g), at 273 K and 298 K respectively]. Interestingly, for the pillared freeze-dried samples, the CO$_2$ uptake at 1 bar as a function of surface coverage, does not follow Vegard's law, meaning that it does not monotonically increases with increasing loading. Instead, it shows a maximum value for the intermediate sample PILGD$_{4,5}$FD, reaching 37 cm$^3$/g (1.65 mmol/g) and 32.9 cm$^3$/g (1.47 mmol/g), at 273 K and 298 K, respectively (Figure 4.10).

The gravimetric uptake is expected to increase with increasing available pore space and decrease with increasing density of the sample. One can anticipate that the insertion of silsesquioxane pillars improves porosity but also makes the material heavier. The lower CO$_2$ uptake of the high loading sample, PILGD$_9$FD [17.9 cm$^3$/g (0.80 mmol/g) at 273 K and 17.8 cm$^3$/g (0.79 mmol/g) at 298 K] suggests that this sample is clogged due to an excess of silsesquioxane pillars. In other words, a high amount of pillars reduces the accessible pore space and increases the density of the material, reducing in this way the CO$_2$ gravimetric uptake. The high CO$_2$ uptake of PILGD$_{4,5}$FD is also supported by the corresponding isosteric heat of adsorption, $Q_{st}$, calculated using the adsorption isotherms at 273 K and 298 K and applying the Clausius–Clapeyron equation. As shown in Figure 4.11, for PILGD$_{4,5}$FD the $Q_{st}$ at zero coverage is 5.7 kJ/mol; it slightly increases up to 7.4 kJ/mol with increasing loading and drops back to 5.4 kJ/mol at high loadings. This behaviour implies the presence of an energetically uniform adsorption environment that favours CO$_2$–CO$_2$ interactions that contributes to high uptake, as has been observed in other porous materials, including MOFs.$^{38}$
Figure 4.10. Gravimetric CO$_2$ uptake at 1 bar of the freeze-dried samples PILGD$_{1.5}$FD, PILGD$_{4.5}$FD and PILGD$_{9}$FD as a function of silsesquioxane loading at the indicated temperatures (up) and the equivalent measurements for the air-dried samples (down)
A diamino-functionalized silsesquioxane pillared GO for CO₂ capture

![Graph showing CO₂ uptake vs. Qₜₐ]

**Figure 4.11.** Isosteric heat of adsorption, Qₜₐ, as a function of surface coverage, for the indicated solids

In contrast, the samples with lower and higher silsesquioxane content both show a rapid decrease of the Qₜₐ values with increasing CO₂ coverage, reaching 2.3 kJ/mol and 0.1 kJ/mol for PILGD₁.₅FD and PILGD₉FD, respectively. Therefore, the average Qₜₐ is significantly lower in both as compared to PILGD₄.₅FD, consistent with the higher CO₂ uptake of the latter. Interestingly, the air-dried samples show a different CO₂ adsorption behaviour, implying a different mechanism of CO₂ sorption in these solids (see Figure 4.9). An uncommon result is that for PILGD₁.₅AD and PILGD₉AD the CO₂ uptake is higher at 298 K than at 273 K, suggesting that CO₂ molecules have better access to the porous space in these solids when their kinetic energy is higher. This can be rationalized considering that these samples have a very compact structure as seen in the SEM images, and therefore a higher kinetic energy (higher temperature) is required for the CO₂ molecules to be able to penetrate between the layers. The fact that PILGD₄.₅AD shows marginally higher CO₂ uptake at 273 K compared to 298 K, could be associated with a less dense packing of the layers in this case, due to optimum silsesquioxane content. For
PILGD$_{4.5}$AD, the calculated $Q_{st}$ drops also fast as a function of surface coverage, reaching 3.3 kJ/mol at high CO$_2$ loading, consistent with the relatively low CO$_2$ uptake 22.0 cm$^3$/g (0.98 mmol/g) at 273 K and 20.4 kJ/mol at 298 K.

4.4. Conclusions

Diamino-functionalised silsesquioxane-pillared graphene oxide structures were synthesized with an easily upscalable protocol, by intercalating reactive silylating agents in the interlayer space between the carbon sheets. We showed that by simply opting for freeze-drying, the preferred drying technique in biology as well as in the pharmaceutical and food industries, the porosity can be significantly enhanced as compared to air-drying. The morphology change induced by freeze-drying can lead to an enhanced CO$_2$ adsorption capacity depending on the loading of the pillaring agent. The CO$_2$ storage capacity of the pillared structures that were developed is relatively high despite their low specific surface area – in general considered one of the key characteristics a highly efficient sorbent material. The pillared structure can compete easily with the performance at ambient conditions of other graphene-based materials possessing much higher specific surface areas ranging from 500 to 1000 m$^2$/g.$^{39}$
A diamino-functionalized silsesquioxane pillared GO for CO$_2$ capture

References


