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Adsorption of CO$_2$ on amine-functionalised MCM-41: experimental and theoretical studies
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Adsorption of CO$_2$ on MCM-41 functionalised with [3-(2 aminoethylamino)propyl] trimethoxysilano (MCM-41-N2), N$_2$-(3-trimethoxysilylpropyl)diethylenetriamine (MCM-41-N3), 4-aminopyridine (MCM-41-aminopyridine), 4-(methylamino)pyridine (MCM-41-methylaminopyridine) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (MCM-41-guanidine) was investigated. The amine-functionalised materials were characterised by $^{29}$Si and $^{13}$C solid-state nuclear magnetic resonance, N$_2$ adsorption/desorption isotherms, X-ray diffraction and transmission electron microscopy. CO$_2$ adsorption at 1.0 bar and 30°C showed that the amount of CO$_2$ (n$_{CO_2}$/mmol g$^{-1}$) adsorbed on MCM-41-N2 and MCM-41-N3 is approximately twice the amount adsorbed on MCM-41. For MCM-41-aminopyridine, MCM-41-methylaminopyridine and MCM-41-guanidine, the CO$_2$ adsorption capacity was smaller than that of MCM-41 at the same conditions. The proton affinity (computed with wB97x-D/6-311++G(d,p)) of the secondary amino groups is higher than that of the primary amino groups; however, the relative stabilities of the primary and secondary carbamates are similar. The differential heat of adsorption decreases as the number of secondary amino groups increases.

Introduction

To satisfy the increasing demand for energy due to population and economic growth, industrial processes and fossil fuel combustion have released an unprecedented amount of CO$_2$ into the atmosphere. The following sectors are mainly responsible for CO$_2$ emissions: energy supply (47%), industry (30%), transportation (11%) and buildings (3%). In the past decade, CO$_2$ concentrations in the range of 430–530 ppm by the end of this century. To reach this level, special attention needs to be given to the carbon energy supply sector, particularly coal-fired power plants. Therefore, the search for efficient methods for the large-scale capture and separation of CO$_2$ from fossil fuel power plants, refineries, oil and gas extraction sites is a challenge that needs to be addressed to reduce CO$_2$ emissions into the atmosphere. 1,2

The current technology based on aqueous alkanolamine solutions, such as 2-aminoethanol (MEA), 2,2-iminodiethanol (DEA), 2,2-methyliminodiethanol (MDEA), 1-(2-hydroxypropylamino)propan-2-ol (DIPA), and 2-amino-2-methylpropan-1-ol (AMP), for CO$_2$ removal was established in 1990.3,4 However, issues related to the high costs and environmental impacts of these alkanolamine solutions due to the corrosive nature of the amines, high regeneration energy in the CO$_2$ stripping step and formation of nitrosoamines (carcinogens) due to amine thermal decomposition are among the biggest challenges of this technology. An alternative to aqueous alkanolamine solutions can be to graft amines (primary, secondary or tertiary) onto solid supports, such as mesoporous silica nanoparticles (MCM-41, SBA-15),3,6,7 zeolites,8 Metal Organic Frameworks (MOFs),9 TiO$_2$,10 and clays.11 This approach is particularly interesting for CO$_2$ uptake at low partial pressures. In addition, it can reduce the energy costs in the CO$_2$ stripping step and also the carcinogenic products resulting from the amine thermal degradation can be avoided.12 MCM-41 is a particularly interesting support to attach amines to either by impregnation or post-synthetic grafting because of its high surface area (~1000 m$^2$ g$^{-1}$), high pore volume (~1.07 cm$^3$ g$^{-1}$), regular pore size (~3.0 nm) and ease of surface functionalisation.13,14,15 Several papers have reported that MCM-41 and pore-expanded MCM-41 have been modified with primary, secondary, tertiary and polyamines.5,16 Sayari et al.16 showed that primary amines anchored onto pore-expanded MCM-41 had higher CO$_2$ adsorption capacity than secondary amines, whereas the tertiary ones barely reacted. This result is interesting because the basicities of secondary and tertiary amines are higher than that of...
the primary ones. Svendsen et al.\textsuperscript{17,18} showed that the reaction between CO\textsubscript{2} at low loadings and an aqueous solution of 2-(2-aminoethyl) amino)-ethanol (H\textsubscript{2}N(CH\textsubscript{2})\textsubscript{2}NH(CH\textsubscript{2})\textsubscript{2}OH, AEEA) – which has one primary and one secondary amine groups in its structure – yielded mainly the primary carbamate of AEEA. The secondary carbamate and the dicarbamate of AEEA were detected in negligible amounts. They concluded that the primary group reacts faster than the secondary group. Monte Carlo simulation of amine-functionalised silica materials indicated that both chemisorption and physisorption processes play a role in the interaction of CO\textsubscript{2} with the surface and that functionalisation makes the CO\textsubscript{2}-surface interaction stronger.\textsuperscript{19}

Previously, using the CAM-B3LYP/6-311++G(2d,2p) approach, we have investigated the interaction between CO\textsubscript{2} and a set of primary, secondary and tertiary amines to form a zwitterion intermediate. We found an almost linear correlation between the CO\textsubscript{2} interaction energies and the amine basicities.\textsuperscript{20} In this work, the synthesis, characterisation, CO\textsubscript{2} uptake and CH\textsubscript{4} uptake by a set of amines anchored onto commercially available MCM-41 are discussed. The relationship between amino efficiency, differential heat of adsorption and basicity (calculated using wB97x-D/6-3111++G(d,p) method) for some of those anchored amines are provided.

**Experimental**

**Materials**

The following chemicals were used with no further treatment: [3-(2-aminoethylamino)propyl]trimethoxysilane, (N\textsubscript{2}-(3-trimethoxysilylpropyl)dienylethenetriamine, (3-chloropropyl)triethoxysilane, 4-aminopyridine, (methylamino)pyridine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (guanidine), triethylamine, benzophenone and sodium hydride from Sigma-Aldrich, dichloromethane and diethyl ether from Vetec-Brazil. MCM-41 mesoporous silica from Sigma-Aldrich, toluene and tetrahydrofuran (THF) from Vetec-Brazil were dried over molecular sieves prior to their use.

**Organoalkoxysilane grafting**

MCM-41 was grafted with [3-(2-aminoethylamino)propyl]trimethoxysilane, N\textsubscript{2}-(3-trimethoxysilylpropyl)dienylethenetriamine and (3-chloropropyl)triethoxysilane by a post-synthesis method\textsuperscript{5,13,14} to give the title compounds MCM-41-N2, MCM-41-N3 and MCM-41-Cl, respectively. Briefly, 6 mL of each organoalkoxysilane was added dropwise to a suspension of MCM-41 (6.00 g) in anhydrous PhMe under reflux (150 mL) in an Ar atmosphere, while stirring vigorously. After 1.5 h, a fraction of 7.0 mL of PhMe containing MeOH or EtOH was distilled off from the suspension, followed by the addition of 3 mL more of each organoalkoxysilane. This procedure was repeated three times, and the reaction mixture was left to stir under reflux and an Ar atmosphere for an additional 24 h. For the MCM-41-Cl compound, this procedure was repeated four times and the suspension heated under reflux for an additional 48 h. The reaction mixtures were cooled to RT, and the resulting suspensions filtered and the excess non-reacted organoalkoxysilane removed by washing the solids in a Soxhlet apparatus using CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O (1:1, 600 mL) for 24 h. The compounds were then dried under vacuum to afford MCM-41-N2, MCM-41-N3 and MCM-41-Cl, as white solids.

**Functionalisation of MCM-41-Cl with 4-aminopyridine, 4-(methylamino)pyridine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (guanidine)**

4-aminopyridine (1.0 g, 10.6 mmol) in anhydrous PhMe (5.0 mL) was added to a suspension of MCM-41-Cl (2.0 g) in dry PhMe under reflux (50 mL) and Ar atmosphere while stirring vigorously. After the reaction mixture had been left to stir for 24 h, it was cooled to RT, filtered and the solid subsequently washed in a Soxhlet apparatus using 5\textsubscript{\%} triethylamine in CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O (1:1, 600 mL) for 24 h and then CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O (1:1, 600 mL) for an additional 24 h. This procedure was necessary to activate the material because upon the nucleophilic substitution, the HCl product remains on the solid surface, neutralising the active site. After this treatment, the material was dried under vacuum and named MCM-41-aminopyridine.

For the synthesis of MCM-41-methylaminopyridine, a solution of 4-(methylamino)pyridine (0.50 g, 4.6 mmol) in 3 mL of anhydrous THF was added dropwise to a suspension of NaH (0.177 g, 7.4 mmol) in 3 mL of tetrahydrofuran (THF) in an ice bath under argon. The suspension was stirred for an additional 2 h at room temperature and then MCM-41-Cl (0.62 g, 0.54 mmol of chlorine) in 4 mL of anhydrous THF was added. The reaction mixture was subsequently heated to 70 \textdegree C under an argon atmosphere for 15 h. Upon cooling to RT, the suspension was filtered and the solid subsequently washed in a Soxhlet apparatus using CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O (1:1, 600 mL) for 24 h. The compound was then dried under vacuum at 80 \textdegree C for 4 h to afford MCM-41-methylaminopyridine.

The synthesis of MCM-41-guanidine has been described elsewhere.\textsuperscript{13}

**Characterisation**

Solid-state \textsuperscript{13}C and \textsuperscript{29}Si NMR spectra were obtained on a Bruker Avance III spectrometer (9.4T), operating at Larmor frequencies of 100.62 and 79.48 MHz, respectively, and equipped with a 4 mm Bruker CPMAS probe and ZrO\textsubscript{2} rotors, spinning at 10 kHz \textsuperscript{(\textsuperscript{13}C and \textsuperscript{29}Si). For \textsuperscript{1}H NMR spectra, a \textsuperscript{1}H-\textsuperscript{13}C cross polarisation magic angle spinning (CPMAS) pulse sequence was employed, with an optimised contact time of 4 ms, and a repetition time (D1) of 1 s. \textsuperscript{29}Si MAS NMR spectra were acquired by using both \textsuperscript{1}H-\textsuperscript{29}Si cross polarisation (CPMAS) with a contact time of 4 ms and direct polarisation, with high power \textsuperscript{1}H dipolar decoupling (HPDD) pulse sequences. In the latter case, the experiments were performed by using repetition times of 10 to 300 s. External references: adamantane for \textsuperscript{13}C and the Q\textsuperscript{3} Si sites of kaolinite at –91.5 ppm for \textsuperscript{29}Si.\textsuperscript{5,13,14}

The amounts of carbon, nitrogen and hydrogen were obtained in a Perkin Elmer CHN 240C analyser, and the amount of chlorine in the MCM-41-Cl sample was determined by the volumetric method at the Analytical Centre of the Institute of Chemistry, University of São Paulo, Brazil.
vacuum for 2 h at 100 °C. X-ray diffraction (XRD) was carried out on a Bruker AXS D8 Advance (Cu Kα radiation, 40 kV and 40 mA). Transmission electron microscopy (TEM) micrographs were acquired using a Carl Zeiss CEM-902 microscope equipped with a Casting-Henry-Ottensmeyer filter spectrometer.

Gas adsorption and calorimetry

The adsorption of methane and carbon dioxide was performed at 30 °C and up to 30 bars. The adsorption isotherms were obtained using a homemade built high-throughput instrument.\textsuperscript{22} Gas adsorption is measured on six samples in parallel via a manometric gas dosing system. The amounts of gas adsorbed are calculated by an equation of state using the Reference Fluid Thermodynamic and Transport properties (REFPROP) software package 8.0 of the National Institute of Standards and Technology (NIST).\textsuperscript{22} Around 100 mg of sample is used, and each sample is thermally activated individually in situ under primary vacuum at a chosen temperature overnight prior gas adsorption measurement. The gases were obtained from Air Liquide: methane was of 99.9995% purity (N55) and carbon dioxide was of 99.995% purity (N45).

The calorimetry experiments were performed using a manometric adsorption apparatus coupled with a Tian-Calvet type microcalorimeter (Setaram, C80). This experimental device allows the determination of the adsorption isotherm and the adsorption enthalpy simultaneously using a point-by-point introduction of gas to the sample. The gas is introduced via a double pneumovalve system into the reference volume. Once the pressure is stabilised in this volume, a pneumovalve is opened to allow the gas to reach the sample. Each introduction of adsorbate to the sample is accompanied by an exothermic thermal effect, until equilibrium is attained. The peak in the curve of energy with time has to be integrated to provide an integral (or pseudo-differential) molar enthalpy of adsorption for each dose. Experiments were carried out at 303 K and up to 30 bars. Approximately 500 mg of the samples were placed in a clean, properly dried high pressure vessel. To compensate for phenomena linked to the vessel and to the injection of gas, a high pressure vacuum vessel was placed in the reference well of the calorimeter.

DFT calculations

To simulate the basicity of the primary versus the secondary amino groups, the relative proton affinities of the N\textsubscript{1}-ethylthylamine-1,2-diamine (CH\textsubscript{x}NH\textsubscript{y}CH\textsubscript{z}N) and N\textsubscript{1}(2-aminoethyl)-N\textsubscript{2}-ethylthylamine-1,2-diamine (CH\textsubscript{x}NH\textsubscript{y}CH\textsubscript{z}NCH\textsubscript{y}CH\textsubscript{z}N) were calculated. The relative energy was also computed for the formation of the carbamate in both the primary and secondary positions of the same amines. Geometry optimizations and calculation of absolute energies were performed with the wB97x-D/6-311++G(d,p) combination of functional\textsuperscript{23} and basis set, using the G09 suite of programs.\textsuperscript{24} To identify the most probable conformation of each protonated amine and carbamates we employed the conformer distribution routine of the Spartan’10 software.\textsuperscript{25} The three most stable conformations of each molecule were then fully optimized with the wB97x-D/6-311++G(d,p) method. Calculation of the second order hessian matrix confirmed all the optimized geometries as a true minimum.

Results and discussion

Chemical modification of MCM-41

The synthetic routes to obtain the functionalised materials containing primary, secondary and tertiary amino groups covalently bounded to MCM-41 are outlined in Scheme 1. Commercially available MCM-41 was modified by a post-synthetic method using [3-(2-aminomethylamino)propyl]trimethoxysilano and N\textsubscript{1}(3-aminomethylamino)propyl(dietylenetriamine) to obtain MCM-41-N\textsubscript{2} and MCM-41-N\textsubscript{3}, respectively (Scheme 1). In this method, the silanols groups that are inside the pores and those on the outer surface are both chemically accessible and may easily react with alkoxysilane derivatives to introduce organic functionality onto the MCM-41. To avoid autocondensation of the alkoxysilanes, the reaction was carried out under anhydrous conditions, and the excess unreacted alkoxysilanes were removed by washing the solids in a Soxhlet apparatus. This procedure was conducted to ensure that only covalently bounded amino groups would be grafted on the MCM-41. The MCM-41-aminopyridine, MCM-41-methylaminopyridine and MCM-41-guanidine materials were obtained by bimolecular nucleophilic substitution reactions (SN\textsubscript{2}) between the MCM-41-Cl and the respective amines, Scheme 1.

Characterisation of the amine-functionalised materials

The \textsuperscript{29}Si CPMAS NMR spectrum of MCM-41 (Fig. 1) exhibits signals at ~92 and ~100 ppm that are associated with the silanols groups SiO\textsubscript{2}(OH)\textsubscript{2} (Q\textsuperscript{2} sites) and SiO\textsubscript{2}-OH (Q\textsuperscript{3} site), respectively.\textsuperscript{5,13,14} A signal at ~113 ppm, associated with the siloxane group SiO\textsubscript{2} (Q\textsuperscript{2} site), was also observed. In addition to the Q\textsuperscript{4}, Q\textsuperscript{2} and Q\textsuperscript{2} sites, all the amine-functionalised materials also exhibit T\textsuperscript{4}, (C-Si(OSi\textsubscript{3})\textsubscript{3}) and T\textsuperscript{2}, (C-Si(OSi\textsubscript{2})\textsubscript{2}OH), sites in the range of ~63 to ~75 ppm and ~62 to ~54 ppm, respectively. T\textsuperscript{0} sites indicates the presence of organic groups covalently bound to the MCM-41.
The $^{13}$C CPMAS NMR spectra of MCM-41-N2 and MCM-41-N3 present four (C1 (6.8 ppm), C2 (18.3 ppm), C3, C4 (35.7 ppm), C5 (48.0 ppm)) and five (C1 (6.8 ppm), C2 (17.6 ppm), C3 (36.4 ppm), C4, C5, C6 (43.6 ppm), C7 (48.0 ppm)) signals, respectively (Fig. 2). In these spectra, C1 is the most shielded by being directly bound to the silicon atom whereas C3, C4 (MCM-41-N2) and C4, C5 and C6 (MCM-41-N3) are assigned to the carbon atoms bound to the amino groups (NH and NH$_2$), following the literature assignments for MCM-41 functionalised with an organoalkoxysilane by the co-condensation method. One signal approximately 162 ppm was assigned to the formation of carbamate, probably due to the reaction of atmospheric CO$_2$ with amino groups anchored onto the surface of the materials.

For the MCM-41-methylaminopyridine, signals related to the aliphatic carbons are observed at 5.9 ppm (C1), 21.6 ppm (C2) and 57.3 ppm (C3). For MCM-41-methylaminopyridine, the aliphatic carbons are observed at 6.5 ppm (C1), 22.5 ppm (C2), 43.9 ppm (C3) and 57.7 ppm (C7). The signals at a higher field, associated with the aromatic carbons, are observed at 139.6 ppm (C4), 107.5 ppm (C5) and 153.4 ppm (C6). The MCM-41-guanidine spectrum was already assigned before.

$^{29}$Si CPMAS NMR spectra of MCM-41 and amine-functionalised samples.

N$_2$ sorption experiments were performed to evaluate the pore features of MCM-41 and their changes upon post-synthetic functionalisation (Fig. 3 and Fig. S1, see ESI†). Fig. 3 shows typical type IV isotherms for MCM-41, MCM-41-N2 and MCM-41-N3. The isotherms for MCM-41-N2 and MCM-41-N3 show a significant reduction of the pore volume but the same type IV feature as that of non-functionalised MCM-41, indicating that upon functionalisation the ordered structures of MCM-41 remain. In contrast, very low surface areas for MCM-41-methylaminopyridine, MCM-41-methylaminopyridine and MCM-41-guanidine (Table 1) were obtained, suggesting that the mesoporous structure of MCM-41 might be damaged or that the pores were completely blocked upon functionalisation.

Pore size distributions, calculated from the adsorption branch of the N$_2$ isotherms at 77 K, are presented in Fig. 3 (inset). MCM-41 shows a pore size distribution approximately 2.7 nm; however, for MCM-41-N2 the pore size distribution shifted to smaller values than that of MCM-41. For MCM-41-N3 the pore size distribution shifted toward values smaller than 2.0 nm.
Fig. 3 N$_2$ Adsorption/desorption isotherms of MCM-41, MCM-41-N2 and MCM-41-N3 and BJH pore size distributions (inset) obtained from the adsorption branch of the isotherms.

Table 1 presents the physical properties of MCM-41 and the amine-functionalised materials. Functionalisation inside or outside the pores is expected to reduce the BET surface area, which can be confirmed by the data presented in Table 1. In addition, a reduction in pore volume ($V_p$) and pore diameter ($D_{BJH}$) is an indication that the functionalisation has, at least, partially occurred inside the pores. However, these pores were not completely blocked because the isotherms maintained the type IV features. For MCM-41-aminopyridine, MCM-41-methylaminopyridine and MCM-41-guanidine, the BET surface areas and pore volumes were drastically reduced (Table 1). The nitrogen and chlorine contents are summarised in Table 1.

To confirm whether the mesoporous structure was damaged after functionalisation with 4-aminopyridine and 4-(methylamino)pyridine, as was observed for MCM-41-guanidine,$^{13}$ X-ray diffraction was performed (Fig. 4). The diffractograms of MCM-41, MCM-41-N2 and MCM-41-N3 were also included in Fig. 4 for comparison. The XRD patterns of MCM-41, MCM-41-N2 and MCM-41-N3 show three low-angle reflections typical of a hexagonal array that can be indexed as the (100), (110) and (200) Bragg peaks. Conversely, the XRD patterns of MCM-41-aminopyridine, MCM-41-methylaminopyridine and MCM-41-guanidine show no reflections. The loss of the $d_{100}$ peak indicates that the functionalisation with 4-(methylamino)pyridine damaged the mesoporous structure of MCM-41, probably due to the higher basicity of 4-aminopyridine and 4-(methylamino)pyridine.$^{30}$ The same was observed for MCM-41-guanidine.$^{13}$

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Table 1 Physical properties of the materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$D_{BJH}$ (nm)</th>
<th>N contents (mmol g$^{-1}$)</th>
<th>Amine surface density (amino group/nm$^2$)</th>
<th>CO$_2$ capacity (mmol g$^{-1}$/sorbent)</th>
<th>Amino efficiency (mol CO$_2$/mol N)</th>
<th>ΔH$_{ads}$ (kJ mol$^{-1}$)</th>
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<tbody>
<tr>
<td>MCM-41</td>
<td>856</td>
<td>0.95</td>
<td>2.7</td>
<td>--</td>
<td>--</td>
<td>0.50</td>
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<td>MCM-41-N2</td>
<td>392</td>
<td>0.39</td>
<td>2.5</td>
<td>2.50</td>
<td>3.87</td>
<td>0.96</td>
<td>0.768</td>
<td>--</td>
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<tr>
<td>MCM-41-N3</td>
<td>266</td>
<td>0.24</td>
<td>&lt; 2.0</td>
<td>3.50</td>
<td>7.93</td>
<td>1.01</td>
<td>0.867</td>
<td>--</td>
</tr>
<tr>
<td>MCM-41-Cl</td>
<td>750</td>
<td>0.71</td>
<td>2.6</td>
<td>0.89$^g$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>MCM-41-4-aminopyridine</td>
<td>3.7</td>
<td>0.02</td>
<td>N. A$^g$</td>
<td>2.00</td>
<td>--</td>
<td>0.07</td>
<td>--</td>
<td>--</td>
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<tr>
<td>MCM-41-methylaminopyridine</td>
<td>8</td>
<td>0.04</td>
<td>N. A$^g$</td>
<td>0.50</td>
<td>--</td>
<td>0.36</td>
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<tr>
<td>MCM-41-guanidine</td>
<td>1</td>
<td>0.00</td>
<td>N. A$^g$</td>
<td>1.70</td>
<td>--</td>
<td>0 40</td>
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</table>

$^a$Data from ref. 5. $^b$Calculated from the adsorption branch using the BJH method. $^c$CO$_2$ capacity obtained at 30 ºC and 1 bar. $^d$Obtained at zero coverage. $^e$The molar capacity was normalised to the number of N atoms present in each molecule. $^f$Cl content (mmol g$^{-1}$) determined from volumetric method. $^g$N. A. – not available

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Fig. 4 X-ray diffraction patterns for MCM-41 and amine-functionalised samples.
CO₂ and CH₄ adsorption and calorimetry

It is well known that amino groups anchored onto mesoporous materials can improve CO₂ adsorption capacity due to acid–base interactions between CO₂ and the amino groups immobilised onto the external surface or within the pores of the solid material. CAM-B3LYP/6-311++G(2d,2p) calculations for the same set of amines we anchored onto the MCM-41 surface showed an almost linear correlation between the CO₂ interaction energies and the amine basicities to form the zwitterion. The stronger bases showed higher interaction energies with CO₂. For the same set of amines investigated in the present work, we would expect to find different behaviour among them towards CO₂ sorption.

The CO₂ and CH₄ isotherms recorded at 30 °C for MCM-41 and for the amine-functionalised materials are presented in Figs. 5 and 6. At high pressures, all amine-functionalised materials show lower CO₂ sorption capacity than that of MCM-41 (Fig. 5). This is probably due to the reduction of the pore volume of the functionalised materials which could increase the resistance to CO₂ diffusion into the pores of these materials. Therefore, in the high-pressure regime, the isotherms reflect a physical adsorption of CO₂. In contrast, at low pressures MCM-41-N2 and MCM-41-N3 show higher CO₂ sorption capacity than either MCM-41 or the other amine-functionalised materials. At 1.0 bar, the amount of CO₂ (n_{CO₂}/mmol g⁻¹) adsorbed onto MCM-41-N2 and MCM-41-N3 is approximately twice the amount adsorbed onto MCM-41 (Table 1). In the amino-functionalised materials, the higher CO₂ adsorption capacity is due to the reaction of this molecule with the basic amino groups anchored onto MCM-41. Thus, the isotherm profiles in this region could be due to both physisorption and chemisorption processes of CO₂. In contrast, MCM-41-aminopyridine, MCM-41-methylaminopyridine and MCM-41-guanidine present a smaller CO₂ adsorption capacity than MCM-41. This result may reflect the fact that the mesoporous structures of MCM-41-aminopyridine, MCM-41-methylaminopyridine and MCM-41-guanidine were destroyed upon functionalisation and, most importantly, after CO₂ adsorption, there would be no acidic hydrogen to be transferred to a second amine, as required by the accepted mechanism. Although MCM-41-aminopyridine has one secondary amino group, its basicity is too low to interact with CO₂. Thus, we will focus our discussion on the CO₂ adsorption capacities of MCM-41-N2 and MCM-41-N3 and compare them with MCM-41-NH₂ (aminopropyl), which was previously published.

The sorption behaviour of the amino-functionalised materials was also evaluated towards CH₄ (Fig. 6). As expected, pure MCM-41 has greater affinity for CO₂ than for CH₄ (Figs. 5 and 6). This may be attributed to either the higher quadrupole moment of CO₂ or the formation of hydrogen bonds between CO₂ and the silanol groups (Si-OH) of MCM-41. The same behaviour was observed for amine-functionalised materials, but the amount of CH₄ adsorbed was less than with MCM-41. Therefore, MCM-41-N2 and MCM-41-N3 could be used to trap CO₂ from natural gas at low pressures.

To assess the CO₂ capture performance by the amine-functionalised materials prepared in this work, the amino efficiency was determined at 1 bar of CO₂, Table 1. The amino efficiency has been defined as the number of moles of CO₂ adsorbed per mole of amino groups and gives an indication of the fraction of the amino groups anchored onto MCM-41 that chemically interact with CO₂. As MCM-41-N2 and MCM-41-N3 have more than one amino group that could in principle contribute to the molar adsorption capacity, we normalised the amino efficiency to the number of N atoms present in each molecule as performed by Puxty et al. For a monoamine, a maximum value of 0.5 is expected considering that two moles of amine is consumed by one mol of adsorbed CO₂. In our previous work, a value of 0.404 was found for MCM-41.
functionailised with an aminopropyl group. The values higher than 0.5 (Table 1) found for MCM-41-N2 and MCM-41-N3 suggest that more than one amino group is participating in the adsorption process. The behaviour of primary vs. secondary amines towards CO$_2$ adsorption has been investigated by Sayari et al. who showed that secondary monoamines have weaker interactions with CO$_2$ than primary monoamines. Additionally, Mamun et al. showed that at low CO$_2$ loading, primary amines react faster than secondary ones, which could be associated with a lower heat of reaction for the secondary amines. However, Puxty et al. investigated the CO$_2$ adsorption capacity of aqueous amine solutions for 76 different amines and showed that the basic strength or pK$_a$ of the amine will affect how far the reaction can go to products. They also concluded that weak amines will not achieve a total amino efficiency (0.5-1.0) and for polyamines, amino groups with low pK$_a$ values will be only spectators and will not contribute to the overall adsorption capacity.

Differential heats of adsorption were obtained for MCM-41, MCM-41-N2 and MCM-41-N3 (Fig. 7). The maximum heats of adsorption were $-61.6$ kJ mol$^{-1}$ (MCM-41-N2), $-54.6$ kJ mol$^{-1}$ (MCM-41-N3) and $-20$ kJ mol$^{-1}$ (MCM-41). For comparison, we also included the differential heat of adsorption of MCM-41-NH$_2$(aminopropyl) ($-98$ kJ mol$^{-1}$) (Table 1). Differential heats of adsorption decrease as the number of secondary amino groups increases. Upon increasing CO$_2$ pressure, the enthalpies of adsorption of the amine-functionalised materials decrease to a value close to the one obtained for MCM-41. From these data, we can estimate the pressure where the amino groups might be saturated with CO$_2$, which is approximately 3 bars. Thus, at pressures higher than these values, the physisorption process might predominate over chemisorption.

![Fig. 7 Differential heats of adsorption of CO$_2$ for MCM-41, MCM-41-N2 and MCM-41-N3.](image)

**Theoretical studies**

The basicsities of the primary and secondary amino groups of the molecules anchored on MCM-41 in this work were simulated by calculations of the relative proton affinities of N$^\text{2}$-ethylenes-1,2-diamine (CH$_2$CH$_2$NH(CH$_2$)$_2$NH) and N$^\text{1}$-(2-aminoethyl)-N$^\text{2}$-ethylenes-1,2-diamine (CH$_2$CH$_2$NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH), using the wB97x-D/6-311++G(d,p) method (see ESI†, Table S1).

The relative proton affinities of the secondary amino groups are much higher than those of the primary amino groups, indicating that the secondary amino groups would be more effective in the interactions with CO$_2$ molecules. To confirm this hypothesis, we also calculated the relative stabilities of the carbamates resulting from the interaction of CO$_2$ with both the primary and secondary amino groups of the same amines (see ESI†, Table S2). The relative stabilities of the primary and the secondary carbamates are indeed very similar. For N$^\text{2}$-ethylenes-1,2-diamine, the secondary carbamate is 1.8 kJ mol$^{-1}$ more stable than the primary one. For N$^\text{1}$-(2-aminoethyl)-N$^\text{2}$-ethylenes-1,2-diamine, the primary carbamate are more stable than the secondary ones (from the two possible secondary carbamates) by 3.8 kJ mol$^{-1}$ on average (on a 4G basis at 298K).

With such small energy differences between the primary and secondary carbamates, we expect that both could be found in the present systems. The lower energy difference for the carbamates compared to the proton affinity of the secondary amines is probably due to the formation of stabilizing intramolecular hydrogen bonds between the carbamate group and the hydrogen donor amino groups (see ESI†, Table S1 and S2). Thus, the strong intramolecular hydrogen bonds found in both primary and secondary carbamates cause a levelling effect in the relative energy. Therefore, based on the relative energies of the carbamates, the formation of either primary or secondary carbamates in these systems cannot be excluded despite the difference in the basicity of the primary and secondary amino groups.

The reduction of the differential heats of adsorption as the number of amino group increases (Fig. 7) cannot be attributed to different behaviours between the primary and secondary amino groups towards CO$_2$ adsorption because the relative energies of the primary and secondary carbamates are close. Most likely, this reduction might be associated with a simultaneous CO$_2$ adsorption on both amino groups. It is reasonable to assume that the simultaneous CO$_2$ adsorption on both primary and secondary amino groups will release a smaller heat of adsorption than that released for the adsorption on either the primary or secondary amino groups.

**Conclusions**

CO$_2$ and CH$_4$ adsorption studies were conducted using commercially available MCM-41 functionalised with [3-(2-aminoethylamino)propyl]trimethoxysilane, N$^\text{1}$-{(3-trimethoxysilylpropyl)diethylenetriamine, 4-aminopyridine, 4-(methylamino)pyridine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (guanidine). Si and $^{13}$C solid state nuclear magnetic resonances showed that all molecules were covalently bounded onto MCM-41. However, X-ray diffraction and transmission electron microscopy revealed that upon functionalisation the mesoporous structure of MCM-41 was destroyed in MCM-41-guanidine, MCM-41-methylaminopyridine and MCM-41-guanidine. Negligible amounts of CH$_4$ were adsorbed on the amine-functionalised materials. In contrast, CO$_2$ adsorption measurements at 1.0 bar and 30 °C showed that the amount of CO$_2$ (n$_\text{ads}$/mmol g$^{-1}$) adsorbed on MCM-41-N2 and MCM-41-N3 is approximately twice the amount adsorbed on MCM-41. For MCM-41-aminopyridine, MCM-41-methylaminopyridine, MCM-41-guanidine, the CO$_2$ adsorption capacities were smaller than for adsorption on MCM-41 at the same conditions. This result could be related to structural damage of MCM-41 upon...
functionalisation and, most importantly, to the absence of an acidic hydrogen atom in these amines necessary to be transferred to a second amine. The amino efficiency of MCM-41-N2 and MCM-41-N3, normalised by the number of N atoms present in each molecule, showed that both primary and secondary amino groups contribute to the CO₂ adsorption on the materials. The proton affinity, calculated using the wB97x-D/6-31+G(d,p) method, is higher for the secondary amino groups than for the primary ones; however, the stabilities of the primary and secondary carbamates on a ΔG basis are similar, showing that both groups can interact with CO₂. Differential heats of adsorption are −61.6 kJ mol⁻¹ (MCM-41-N2), −54.6 kJ mol⁻¹ (MCM-41-N3) and −20 kJ mol⁻¹ (MCM-41) indicating a chemical interaction between CO₂ and the amine-functionalised materials at low pressures. The differential heat of adsorption decreases as the number of secondary amino groups increases (e.g., for MCM-41 functionalised with aminopropyl group it is −98 kJ mol⁻¹, ref. 5), probably due to simultaneous CO₂ adsorption on secondary and primary amino groups.

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Notes and references


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