

CO₂ adsorption performance of amino-functionalized SBA-15 under post-combustion conditions

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Abstract

Carbon dioxide adsorbents prepared from SBA-15 mesostructured silica functionalized with amino groups have been tested under a simulated gas mixture similar to that of a coal-fired thermal power plant. SBA-15 material was functionalized by grafting with aminopropyl-trimethoxysilane (AP (N)) and diethylene-triamine-trimethoxysilane (DT (NNN)), and by impregnation with polyethyleneimine (PEI) and tetraethylenepentamine (TEPA). CO₂ adsorption performance was measured in both a thermobalance and in a fixed bed. A thorough study of the adsorption behaviour was carried out, including the influence of conditions found in real post-combustion operation processes, such as diluted CO₂ concentration, presence of SO₂ and moisture in the flue gas. The reutilization of the adsorbent by successive adsorption-desorption experiments has also been tested.

Grafted materials and samples impregnated with around 50 % organic amount or higher, showed a small influence of the dilution of CO₂ in the feed gas on their CO₂ uptake. Adsorption capacity after 10 cycles remains almost unaltered for grafted and PEI-impregnated solids and moderately decreases for TEPA-impregnated adsorbent. CO₂ adsorption capacity decreased significantly with the presence of 1,000 ppm SO₂ for up to 5 cycles, finding a direct correlation with the nitrogen content of the sorbents. Humid conditions (5 % moisture) do not significantly affect adsorption capacity of grafted samples, but improve the CO₂ uptake of impregnated adsorbents about 50-60 %, obtaining an adsorption capacity of 16.2 wt. % CO₂ (3.7 mmol CO₂/g) for sample SBA-TEPA (50) in a humid diluted CO₂ stream (15 % CO₂) at 45 °C and 1 bar.

Keywords: Mesoporous silica SBA-15, amino-functionalization, Polyethyleneimine (PEI), Tetraethylenepentamine (TEPA), CO₂ adsorption, SO₂ poisoning

1. Introduction

Amongst CO₂ capture technologies for post-combustion, absorption processes with aqueous amine solutions are widely known and frequently used. However, many drawbacks have been described, especially high energy consumption during the endothermic absorbent regeneration step [DOE, 1999; Tontiwachwuthikul et al., 1991]. As an alternative, porous solids have been investigated as CO₂ adsorbents [Choi et al., 2009; Samanta et al., 2012]. Zeolites and some types of activated carbons physically adsorb noticeable amounts of CO₂ at low temperature and high pressure [Arenillas et al., 2005; Plaza et al., 2007; Wahby et al., 2010; Olivares-Marín et al., 2011]. However, they present a steep drop in CO₂ adsorption capacity at temperatures higher than 25°C or low CO₂ partial pressures, which are typical post-combustion conditions [van der Vaart et al., 2000; Siriwardane et al., 2001]. With the aim of overcoming these problems, hybrid organic-inorganic materials obtained by incorporation of organic groups to an inorganic matrix have been proposed, mesostructured silicas being one of the most promising supports due to their excellent textural properties [Harlick and Sayari, 2007; Xu et al., 2003]. The interaction between basic surface functional groups, generally amino groups, and acid CO₂ molecules, explains the CO₂ capture with these adsorbents, as presented in Scheme 1. According to this mechanism, the maximum achievable CO₂/N molar ratio value is 0.5 under dry conditions and 1.0 in presence of moisture. The molar CO₂ adsorption capacity per mol of nitrogen (mol CO₂/mol N) is often considered as a measure of the adsorbent efficiency in the adsorption process. Due to the reversibility of the reactions, these materials can be regenerated at mild

temperatures (50-100 °C) in TSA processes, VSA processes or a combination of both, whereby pure CO₂ is obtained and the adsorbent is regenerated.

Apart from the CO₂ adsorption capacity and efficiency (CO₂/N molar ratio) of selected adsorbents, it is also necessary that they present appropriate selectivity, reusability and stability in the presence of water and pollutants in the flue gas. For example, the presence of SO₂ is very likely to strongly compete for adsorption sites in CO₂ capture, turning this impurity into a poison for amino-modified porous materials [Choi, 2009].

Scheme 1. Reaction pathway of primary amine groups and CO₂ molecules

The objective of this work is to evaluate the effect of post-combustion conditions typical of the flue gas of a coal-fired thermal power plant, such as CO₂ concentration, presence of SO₂ and moisture and the long-term behaviour of solid sorbents based on mesostructured SBA-15 incorporating molecules containing amino groups. To achieve this objective, aminopropyl-trimethoxysilane (AP (N)) and diethylenetriamino-trimethoxysilane (DT (NNN)) moieties have been incorporated by grafting into SBA-15 silica, while polyethyleneimine (PEI) and tetraethylenepentamine (TEPA) have been added to the structure by impregnation. CO₂ adsorption performance of the resulting materials has been tested under pure CO₂, a “clean” diluted stream (15 % CO₂, 5 % O₂, 80 % N₂), a SO₂-containing gas mixture (15 % CO₂, 1,000 ppm SO₂, N₂ balance) and a diluted gas mixture (15 % CO₂, 5 % O₂, 80 % N₂, dry basis) with aprox. 5 wt. % H₂O for up to 5 adsorption-desorption cycles.

2. Experimental Section

2.1. Synthesis of SBA-15 mesostructured silica

SBA-15 support was synthesized following the original procedure reported by Stucky and co-workers [Zhao et al., 1998]. A large scale synthesis was employed to obtain up to 40 g of SBA-15 by using Pluronic P123 (PEO₂₀-PPO₇₀-PEO₂₀, Mn~5800, Sigma-Aldrich) as structure directing agent and TEOS (tetraethyl orthosilicate, 98 %, Sigma-Aldrich) as silica source [Sanz et al., 2010]. The experimental procedure involved the mixing of Pluronic P123 in 1.9 M HCl and stirring until complete dissolution. Then, TEOS was added to the acidic medium and a hydrolysis step at 40°C for 20 h was carried out. An ageing step at 110°C for 24 h was performed to complete the formation of the SBA-15 hexagonal mesostructure. Finally, the solid was filtered and the surfactant was removed from the porous structure by calcining in air at 550°C for 5 h.

2.2. Functionalization of SBA-15

2.2.1. Grafting

A grafting method was employed to functionalize calcined SBA-15 support with aminopropyl-trimethoxysilane, AP (N) and diethylene-triamine-trimethoxysilane, DT (NNN) (acquired from Sigma-Aldrich), according to the following procedure: the organosilane was added to a dispersion of 1 g of SBA-15 material in 250 mL of toluene. The mixture was stirred under reflux for 24 h and the solid obtained was filtered and washed with 200 mL of toluene in order to remove the excess of non reacted organosilane. As previous studies determined that air-drying of amino-grafted solids at 110 °C leads to the formation of carbonyl bonds [Calleja et al., 2011], with no reactivity towards CO₂, the obtained materials were dried at room temperature overnight. Synthesized samples were named SBA-15-AP (N)-6 and SBA-15-DT (NNN)-6, where

6 represents the hypothetical surface concentration of silanol groups over SBA-15 pore walls (6 SiOH/nm^2), chosen in a previous study [Calleja et al., 2011]. Taking into account the surface area value obtained for SBA-15 and a 1:1 reaction between surface silanol groups and organosilane molecules, the corresponding amount of organosilanes added was $6.89 \text{ mmol org/g SBA-15}$.

2.2.2. Impregnation

Impregnation of calcined SBA-15 was carried out with polyethyleneimine (PEI, branched polyethyleneimine, average molecular weight 800, $\rho = 1.05 \text{ g/mL}$) and tetraethylenepentamine (TEPA, $\rho = 0.998 \text{ g/mL}$), both from Sigma-Aldrich. A wet impregnation procedure was used to obtain 2 g of each adsorbent material. The procedure was as follows [Xu et al., 2003]: the desired amount of the organic compound was dissolved in methanol (methanol/SBA-15 = 8). Then, the corresponding amount of SBA-15 was added and the mixture was stirred for 30 min. The resulting final solid was dried at room temperature overnight, to avoid amino group degradation. Synthesized samples were named SBA-15- x (y), where x stands for the functionalization agent employed (either PEI or TEPA) and y represents the organic weight percentage in the final material, ranging from 10 to 70 %.

2.3. Characterization of materials

2.3.1. Physico-chemical characterization

Low angle XRD diffractograms of the synthesized samples were acquired with a powder diffractometer PHILIPS X-PERT MPD using the $\text{CuK}\alpha$ monochromatic radiation. Nitrogen adsorption-desorption isotherms at 77 K were performed in a Micromeritics Tristar-3000 sorptometer. SBA-15 silica was outgassed at $200 \text{ }^\circ\text{C}$ in N_2 flow for 8 h, while functionalized samples outgassing temperature was decreased to

150 °C in order to preserve the organic loading. B.E.T. equation was used to determine surface area values (P/P_0 between 0.05 and 0.20), pore size distributions were obtained from the adsorption branch of the isotherm by using the B.J.H. model assuming cylindrical pore geometry, and pore volume was taken at $P/P_0 \geq 0.97$ [Sing et al., 1985]. Elemental analyses of carbon, nitrogen and hydrogen were carried out in a Thermo Flash EA 1112 analyzer equipped with an MAS 200R autosampler.

2.3.2. Adsorption of CO₂

Pure CO₂ adsorption measurements were performed with a thermal gravimetric analyzer Q500, TA Instruments apparatus. Samples were pre-treated to remove moisture and adsorbed gases by heating up to 110 °C under a nitrogen flow of 100 mL/min for 2 h. After that, the temperature was decreased to the adsorption conditions and subsequently CO₂ was introduced. With the aim of thoroughly testing the performance of amine-functionalized SBA-15 for CO₂ adsorption, several measurements were conducted: pure CO₂ adsorption versus temperature (thermogravimetric analyses under flux of pure CO₂), CO₂ adsorption versus time and multi-cycle of CO₂ adsorption tests. The last two types of experiments were carried out with pure CO₂, a clean gas mixture (15 % CO₂, 5 % O₂, 80 % N₂) with a CO₂ content similar to that found in the flue gas of coal-fired thermal power stations [Tzimas and Peteves, 2003], and a sulphur-containing gas mixture (15 % CO₂, 1,000 ppm SO₂, N₂ balance), with a SO₂ content much higher than the maximum level of 162-810 ppm established by the European Union for these facilities [E.P.C., 2001]. Inlet gas flow was maintained at 100 mL/min regardless of the mixture composition. Equilibrium times were of 3 h for single-point measures, while dynamic tests were carried out with a heating rate of 0.5 °C/min.

A fixed bed reactor (PID Eng & Tech Microactivity-Reference, 0.91 cm inner diameter, 10 cm length) was used to perform cyclic adsorption measurements with a CO₂ diluted

stream (15 % CO₂, 5 % O₂, 80 % Ar, dry basis) of 100 mL/min with a water content of 5 wt. %. The samples were pre-treated before each adsorption cycle by heating up to 110 °C under 100 mL/min Ar for 2 h to remove moisture and adsorbed gases. After that, the temperature was decreased to 45 °C and subsequently, the gas mixture was introduced. Contact times of 30 min were enough to reach the saturation of studied materials. Desorption was performed in two steps, by using a pure argon stream of 100 mL/min during 30 min at 45°C and additionally during 2 h at 110 °C.

CO₂ adsorbed amount was measured with a mass spectrometer (Pfeiffer Vacuum QMG220) coupled to the fixed bed. A blank analysis with glass pearls was used to calculate the void volume due to the tubing and the interparticle space. Breakthrough curves (q_{CO₂} vs time) were integrated to calculate the CO₂ adsorbed volume. Up to 500 mg of sample was used for fixed bed experiments.

3. Results and discussion

3.1. Physico-chemical characterization

SBA-15 siliceous support as well as aminopropyl, AP (N), and diethylenetriamine, DT (NNN), grafted materials and samples impregnated with increasing amounts of polyethyleneimine, PEI, and tetraethylenepentamine, TEPA, were characterized by low angle X-ray diffraction and the diffractograms are shown in Figure 1. The SBA-15 mesostructured material presented the distinctive diffraction peaks of a two-dimensional hexagonal mesostructure [Zhao et al., 1998]. After functionalization either by grafting (Figure 1a) or by impregnation with TEPA (Figure 1b) and PEI (Figure 1c), the adsorbents exhibited the same diffraction pattern. However, the intensity of the peaks gradually decreased as the chain length was increased for grafted samples, or as the organic content was increased for the impregnated ones. This behaviour is related to the

filling of pores with organic compounds, which avoids the X-Ray diffraction through the mesoscopic structure. Nevertheless, SBA-15 porous structure was preserved after any of the functionalization processes.

Fig. 1. Low angle X Ray diffractograms for pure SBA-15 before and after functionalization by a) grafting with AP (N) and DT (NNN) or impregnation with b) TEPA and c) PEI

N₂ adsorption-desorption isotherms and pore size distributions of siliceous and functionalized samples are presented in Figure 2. Textural properties and nitrogen content of the synthesized materials are listed in Table 1. SBA-15 mesostructured support presented a Type IV isotherm according to the IUPAC classification [Sing et al., 1985], combining the presence of micro and mesoporous. This siliceous material exhibited characteristic values of surface area (587 m²/g), pore diameter (8.5 nm) and pore volume (0.96 cm³/g).

Nitrogen adsorbed amount and textural properties of functionalized materials decreased due to the extent of the pore filling resulting from the functionalization. These observed changes were more pronounced both for longer organosilane chains in grafted materials and for higher loadings of the molecule in the impregnated materials. As an example, SBA-15-AP (N)-6 and SBA-15-DT (NNN)-6 adsorbents, which contain 3.7 and 5.3 % nitrogen respectively, presented surface areas of 286 and 227 m²/g, mean pore diameters of 7.1 and 6.8 nm, and pore volume values of 0.50 and 0.39 cm³/g, respectively.

Fig. 2. N₂ adsorption-desorption isotherms at 77 K for pure SBA-15 and functionalized samples by a), b) grafting with AP (N) and DT (NNN) or impregnation with c), d) PEI and e), f) TEPA.

The loading of organosilane in the grafting process depends on the specific area of the material and on its silanol surface concentration. As shown in the isotherms in

Figure 2a, a significant fraction of the pore volume remained unfilled even with high organic loadings, due to the high ratio pore diameter/organosilane chain. In contrast, when the impregnation method was used, the extent of the organic functionalization did not depend on the number silanol groups, as the total pore volume is the only limitation in this case. Thus, the organic amount loaded by this method may completely fill the pores, saturating the support, as it happens with SBA-15-PEI (70), whose nitrogen adsorption capacity is negligible.

Pore size distributions for functionalized materials experimented a broadening and a shift to lower pore diameters as pores were filled with organic compounds, as observed in Figure 2.

Table 1. Textural properties and nitrogen content of siliceous SBA-15 and amine-functionalized samples

The nitrogen content of the functionalized samples is also shown in Table 1. As expected, this value increased for longer grafted organosilane chains and for higher impregnated organic quantities. The higher loading achieved by impregnation rather than by grafting observed in the N₂ adsorption isotherms is verified by their respective nitrogen content, ranging from 3.1 to 20.8 % for impregnated materials, versus 3.7-5.3 % for grafted samples. Among impregnated samples, the use of PEI led to a nitrogen content of 3.4-16.6 %, while the use of TEPA resulted in materials with a nitrogen content ranging 3.6-20.8 %. This increment is related to the higher nitrogen content per molecule in the case of TEPA (49.6 %) comparing to PEI (36.8 %).

3.2. CO₂ adsorption

3.2.1. Influence of temperature

The influence of temperature on the CO₂ adsorption behaviour was studied by thermogravimetric dynamic analyses. After saturating each sample in a pure CO₂ flow at 25 °C for 3 h, the temperature was raised up to 200 °C with a slow heating rate of 0.5 °C/min. The variation of CO₂ uptake with the temperature was registered for SBA-15 siliceous support, grafted adsorbents and samples impregnated with 50 % organic content (Figure 3). Table 2 lists CO₂ adsorption capacities calculated from the mass gain at 25 °C (q_{25} , equilibrium data) and 110 °C (q_{100} , extracted from the dynamic test, equilibrium was not reached). Besides, the ratio q_{25}/q_{100} has been calculated in order to compare the influence of the temperature on the CO₂ adsorption uptake.

As observed, pure SBA-15 presented a low CO₂ adsorption capacity (1.42 wt. % at 25 °C). When the temperature was increased, a noticeable drop in the CO₂ uptake was registered, the adsorption uptake being reduced to 0.12 wt. % at 110 °C, which represents just 8.3 % of the measured CO₂ adsorption capacity at 25 °C. This tendency is typical of physisorption-like processes, where adsorbate uptake constantly diminishes as the temperature rises. Physical adsorbents present a significant adsorption capacity at high pressure and low temperature, but their performance at moderate temperature and low pressure (as needed for post-combustion capture) is normally quite poor.

Thermogravimetric analyses for AP (N) and DT (NNN) grafted samples are also shown in Figure 3a. CO₂ uptake at 25 °C (6.18 and 7.66 % CO₂) was considerably higher than the obtained for the siliceous support (1.42 % CO₂) and showed a dependence on the nitrogen content of the material, as the reaction between amine groups and CO₂ follows the mechanism shown in Scheme 1 [Caplow ,1968]. After reaching equilibrium at 25 °C, the temperature was increased and a subsequent drop in the CO₂ uptake of grafted materials was registered. This trend was also observed for siliceous SBA-15.

However, the CO₂ adsorption capacity at 110 °C still represents about 33 % of the values achieved at 25 °C by grafted samples, while this percentage was 8.3 % in the case of siliceous SBA-15.

Fig. 3. Pure CO₂ uptake during temperature-programmed experiments for pure SBA-15 support and samples functionalized by a) grafting with AP (N) and DT (NNN) or b) impregnation with 50 % of PEI and TEPA.

The different performance of amine-containing materials with temperature compared to SBA-15 is assigned to the relevant contribution of the chemical adsorption promoted by amino functionalities to the whole CO₂ uptake process. For these functionalized materials, two effects are expected when the temperature is raised. On one hand, CO₂ uptake due to both physical and chemical adsorption decreases when the temperature increases, as they are exothermic processes. On the other hand, NH₂-CO₂ reaction kinetics, mobility of organic molecules and CO₂ diffusion through filled pores are favoured by an increase of temperature.

As the SBA-15 support does not contain any amino groups, its CO₂ uptake is completely due to physical adsorption. Consequently, the value registered at 100 °C is almost nil, resulting in a low q_{25}/q_{100} ratio of 8.3. For grafted materials, the influence of temperature was smaller, as shown by the higher q_{100}/q_{25} ratio obtained (33 %), due to the influence of chemisorption.

At higher temperature (140 °C) grafted materials exhibited a certain CO₂ uptake increase. It can be related to secondary reactions previously reported to form carbonyl bonds at moderate temperatures from the amino moieties present in grafted SBA-15 materials [Calleja et al., 2011, Bollini et al., 2011], and evidenced by the change of colour of the samples from white to pale yellow. Urea moieties have been obtained after heating polyethyleneimine (Drage et al., 2008) and organosilane molecules (Sayari et

al., 2012) at similar temperatures under CO₂. The main drawbacks of these secondary reactions are their irreversibility and the absence of reactivity between CO₂ and the resulting functional groups formed.

Table 2. Nitrogen content and pure CO₂ adsorption capacities at 25 and 110 °C and 1 bar for SBA-15 and amine-functionalized samples

Adsorbents prepared by impregnation with PEI and TEPA presented a different performance compared to grafted materials. The SBA-PEI (50) sample showed an adsorption capacity of 7.58 % CO₂ at 25 °C, similar to those achieved by grafted materials (6.18 and 7.66 % CO₂). Despite the higher nitrogen content of SBA-PEI (50), this sample achieves a similar CO₂ uptake than grafted samples due to the lower efficiency in CO₂ capture (mol CO₂/mol N) of the amino groups contained in the PEI impregnated sample, as previously reported [Sanz et al., 2010]. This behaviour is related to the high organic amount present in the pores of the adsorbent, whose total pore volume is just 0.09 cm³/g, and to the viscous nature of PEI, which hinders CO₂ diffusion and its reaction with amino groups in deeper pore locations. Besides, some of the introduced PEI may be partially deposited in the outer surface, forming a layer of polymer that entails an additional diffusion hindrance [Sanz et al., 2012].

The high nitrogen content of SBA-PEI (50) does have remarkable effects in its temperature-dependent behaviour, as seen in its less pronounced CO₂ uptake decreasing rate with temperature. Adsorption capacities at 25 and 110 °C were 7.58 and 5.10 % CO₂, so the value at 110 °C represented a 67.3 % of the measured CO₂ uptake at 25 °C (ratio q_{100}/q_{25}) for this sample. This parameter takes lower values for grafted samples (*ca.* 33 %) and siliceous SBA-15 (8.3 %), showing that chemical adsorption is

more relevant in the PEI (50) impregnated material. This adsorbent contains a high amount of amino groups, contributing to chemisorption, and its specific surface is lower, reducing the amount of CO₂ physically adsorbed.

The SBA-TEPA (50) impregnated material reached the highest CO₂ adsorption capacity (9.77 wt. % at 25 °C) amongst the samples investigated. This is probably explained by the preponderance of chemisorption over physisorption in this material, due to its nitrogen content (15.4 %, the highest value in this series). Moreover, the accessibility of amino groups in TEPA-impregnated samples could be higher, as TEPA presents a low viscosity that favours its mobility and CO₂ diffusion through filled pores compared to PEI.

Another interesting feature of the sample SBA-TEPA (50) is its adsorption uptake dependence on temperature, as it is the only material to show an increasing tendency with temperature, showing a maximum in the CO₂ adsorption capacity at about 80 °C. Thus, a change in the overall balance of temperature-dependent processes occurs. In consequence, positive effects of a temperature rise (increase of mobility in the pores, reaction kinetics and CO₂ diffusion) exceed the negative effects, related to the exothermic nature of physical and chemical adsorption over amino groups. Therefore, CO₂ adsorption capacity at 110 °C for SBA-TEPA (50) represented up to 83.8 % of the data taken at 25 °C, which is the highest q_{100}/q_{25} ratio amongst the studied samples.

The curves of PEI and TEPA impregnated samples presented a minimum in the CO₂ uptake at around 140 °C. This variation is similar to the observed for grafted materials, as the same NH₂-CO₂ interaction occurs, so that an analogue secondary reaction to form carbonyl bonds was taking place. It must be underlined that a significant mass loss was observed for TEPA-impregnated sample from 100 °C onwards (Figure 3b), that can be due to a certain evaporation of the organic amine employed.

3.2.2. Effect of CO₂ concentration

To evaluate the effect of dilution on the CO₂ adsorption performance of amino functionalized samples, thermogravimetric analyses were carried out with a pure CO₂ stream and a CO₂ diluted stream (80 % N₂, 15 % CO₂, 5 % O₂). AP (N) and DT (NNN) grafted samples and the whole series corresponding to PEI and TEPA impregnated materials were tested.

In view of the thermogravimetric results for TEPA (50) impregnated sample, several degasification temperatures were used prior to measure CO₂ adsorption capacity at 45 °C of TEPA-containing samples. Table 3 shows the dependence of CO₂ adsorption values of SBA-TEPA (50) adsorbent with degasification temperature. As it can be seen, an outgassing temperature increment from 60 to 100 °C led to significant higher CO₂ uptakes in the adsorption process, since a thorough outgassing process resulted in the complete removal of physically adsorbed gases and moisture. Despite that, an increment of the degasification temperature above 100 °C favoured TEPA evaporation and thus subsequent CO₂ adsorption process reached a much lower uptake.

Table 3. Degasification temperature and CO₂ adsorption capacity achieved at 45 °C and 1 bar for SBA-TEPA (50) impregnated sample

CO₂ adsorption measurements were then carried out for grafted and impregnated samples. 110 °C was the degasification temperature for these materials, except for TEPA-containing materials which, as discussed before, need to be outgassed at 100 °C, and moreover, this is the same temperature used by other researchers employing the same adsorbent [Yue et al., 2008]. Table 4 lists the CO₂ adsorption capacity achieved in a pure CO₂ flow and a diluted stream (80 % N₂, 15 % CO₂, 5 % O₂). A temperature of

45 °C was selected to carry out adsorption tests with all the functionalized samples. This value corresponds to the outlet temperature of the flue gas after the desulphurization step in a typical coal-fired thermal power station [Gaikwad et al., 2003].

Despite the registered variable has been the mass uptake and the concentration of individual gases has not been detected, it was assumed that amino-containing materials were completely selective to CO₂ even in an 80 % N₂ stream due to the chemical nature of the interaction between CO₂ and amino groups. However, that was not the case of SBA-15 siliceous material, that adsorbs CO₂ or N₂ only by physical adsorption and, thus, no selective interactions are present. To evaluate the N₂ and CO₂ adsorption capacity of pure SBA-15, several tests in N₂, CO₂ and a mixture N₂-CO₂ (80%-20%) were performed. The mass uptakes for these three experiments were 0.03 %, 0.75 % and 0.17 %, respectively. These adsorption data indicate that pure silica materials present high selectivity towards CO₂. In fact, a CO₂/N₂ ratio of 25/1 is inferred from the pure gas adsorption data for siliceous SBA-15, that may seem too high for a physisorption process in open pores. This result can be explained taking into account the mechanism of physical adsorption, originated by weak intermolecular forces between the adsorptive and the surface of the porous adsorbent. Dispersion and repulsion are nonspecific interactions, i.e. they are present in all gas-solid systems [Barrer, 1978], being also the main forces in all adsorbents. For molecules such as N₂, O₂, H₂, Ar or CH₄, there are no other forces present, since these molecules show no dipole moment and their quadrupole moment is very low or nil [Ross and Olivier, 1964; Steele, 1974; Rudzinski and Everett 1992]. Besides, there exist adsorbent-adsorbate electrostatic interactions (polarization energy, field dipole and field quadrupole energies), which depend on the structure and composition of both the adsorbed molecule and the porous adsorbent, i.e. they are specific interactions. The high quadrupolar moment of CO₂ ($-4.3 \cdot 10^{-42} \text{ C} \cdot \text{m}^2$)

[Buckingham and Disch, 1963], its subsequent higher polarizability, and the possible presence of the adduct $\text{H}^{\delta+} \cdots \delta^- \text{O}=\text{C}=\text{O}^{\delta-}$ weakly bonded to silica surfaces [Roque-Malherbe et al., 2010] result in a specific interaction of CO_2 with most adsorbents. As a consequence, a preferential adsorption of CO_2 and a certain selectivity towards this gas in mixtures with the aforementioned compounds is expected, as we have observed upon here.

For amino-functionalized materials, the selectivity towards CO_2 is higher and more obvious compared to siliceous SBA-15, as chemical adsorption between amino groups and carbon dioxide is the dominant process. For example, the selectivity of PEI-impregnated materials towards CO_2 has been reported to be noticeable, achieving CO_2/O_2 and CO_2/N_2 ratios of 180 and 1,000 respectively (Xu et al., 2004). Therefore, no measures under pure nitrogen were carried out for amino-functionalized samples. It can be accurately assumed that virtually all the mass uptake is due to CO_2 adsorption in all siliceous and functionalized samples presented in this work.

The SBA-DT (NNN)-6, SBA-PEI (50) and SBA-TEPA (50) samples, with a nitrogen content of 5.3, 8.3 and 15.4 % respectively, presented a CO_2 adsorption capacity of 6.69, 7.49 and 11.35 % (Table 4) at 45 °C, while values registered at 25 °C were 7.66, 7.58 and 9.77 % (Table 2). This change is related to the increasing importance of chemical adsorption at higher temperatures, as previously described in section 4.2.1.

The change from pure CO_2 to a diluted mixture (15 % CO_2) generated a different behaviour among studied samples. SBA-15 siliceous support experimented a significant decrease of CO_2 uptake, from 0.75 to 0.17 % CO_2 . For physical adsorbents, the adsorption capacity for a given adsorptive is mainly related to its partial pressure in the gas phase. As the diluted stream contains 15 % CO_2 , the theoretically expected uptake ratio $q_{\text{DIL}}/q_{\text{PURE}}$ is 15 %. In the experiment with the diluted stream, the CO_2 uptake

obtained for SBA-15 was 0.17 %, thus representing a q_{DIL}/q_{PURE} ratio of 22 %. The close theoretical and experimental values confirm that the CO₂ adsorption mechanism for SBA-15 is physical adsorption.

In contrast, functionalized samples achieved a CO₂ adsorption capacity from a diluted mixture much closer to pure CO₂ uptake values, from which the existence of certain selectivity towards CO₂ can be inferred. The selectivity of each sample can be determined by measuring the variation in its mass uptake when using the gas mixture in comparison with the value obtained under a pure CO₂ stream, i. e., the ratio q_{DIL}/q_{PURE} . Table 4 lists these percentages, denoting by 100 % that the same mass uptake was registered under a pure CO₂ stream and under a diluted mixture. As seen, all the functionalized samples showed a certain degree of selectivity towards CO₂, determined by its nitrogen content, showing that the higher the nitrogen content, the greater the influence of chemical adsorption.

Table 4. Gas uptake at 45 °C with pure and diluted CO₂ of amine-functionalized samples

Grafted samples, SBA-AP (N)-6 and SBA-DT (NNN)-6, presented a significant adsorption performance under the diluted mix, achieving a q_{DIL}/q_{PURE} ratio of 70-80 %. This result confirms the contribution of chemical adsorption to the whole process in these materials. However, physical adsorption still presents a significant contribution in these adsorbents, as previously shown by their CO₂ uptake dependence with temperature. This fact explains that the SBA-AP (N) sample, with a nitrogen content of 3.7 %, achieved a q_{DIL}/q_{PURE} ratio of 81 %, much higher than the obtained with impregnated samples SBA-PEI (10) and SBA-TEPA (10), containing a similar nitrogen content (3.4 and 3.6 %, respectively), which presented selectivities of around 50 %.

Samples impregnated with 50 to 70 % PEI and TEPA exhibited higher CO₂ uptake values (ranging 7.49-11.06 % under pure CO₂ at 1 bar and 45 °C), as they present higher nitrogen contents (8.3-20.8 %). PEI and TEPA compounds have different behaviour during the impregnation procedure. The lower viscosity of TEPA is supposed to enhance its way into the pores, whereas PEI polymer has been suggested to hinder CO₂ diffusion and even to be partially deposited on the outer surface of the particles [Sanz et al., 2012]. This different performance led to a higher accessibility of TEPA molecules, and a higher CO₂ uptake than PEI-materials with a similar nitrogen content (more evident for higher loaded samples), for example SBA-PEI (70) (16.6 % N; 9.80 % CO₂) and SBA-TEPA (50) (15.4 % N; 11.35 % CO₂).

The q_{DIL}/q_{PURE} uptake ratios obtained for PEI and TEPA-impregnated adsorbents are similar. This value was low for the less loaded samples (47 and 50 % for SBA-TEPA (10) and SBA-PEI (10), respectively) due to a certain contribution of physical adsorption. As the nitrogen content increases, chemisorption becomes the dominant CO₂ adsorption mechanism, so that CO₂ adsorbed values from the gas mixture progressively reached uptake values of pure CO₂. The highest loaded samples, SBA-PEI (70) and SBA-TEPA (70), presented selectivity values close to the maximum (q_{DIL}/q_{PURE} ratios reach 90-100 %), which means that their CO₂ uptakes under the diluted mixture (15 % CO₂) were very similar to those obtained under pure CO₂, as previously reported [Yue et al., 2008]. Moreover, no side effects were observed because of the 5 % oxygen fed in the gas mixture employed. Hence, these materials stand out as potential CO₂ adsorbents highly capable to treat CO₂ diluted streams, as they show high uptakes (9.00 and 11.47 % CO₂ for SBA-PEI (70) and SBA-TEPA (70), respectively) and selectivities towards this compound (92 and 100 %, respectively).

3.2.3. Adsorption-desorption cycles

Diethylenetriamine (DT (NNN)) grafted sample and materials impregnated with 50 % PEI and TEPA were selected to study their cyclic behaviour by performing up to 10 adsorption-desorption cyclic experiments at 45 °C with pure CO₂ and a diluted stream (80 % N₂, 15 % CO₂, 5 % O₂). Figure 4 displays CO₂ adsorption results for each cycle, expressed as q_i/q_1 , i.e. the ratio between the CO₂ uptake for a certain cycle referred to the first pure CO₂ uptake data for the same sample.

Pure CO₂ cycles (full symbols) show that adsorption capacity was successfully maintained for materials containing DT (NNN) and PEI after 10 cycles (up to 96.9 and 94.5 % respectively in comparison with the first cycle), in accordance with previous studies [Belmabkhout and Sayari, 2010].

The TEPA-impregnated sample underwent a loss in its CO₂ adsorption capacity in the second cycle of the series in comparison with the first experiment. This drop may be assigned to a partial evaporation of TEPA, while organic evaporation is negligible for DT (NNN) grafted sample, where the organic groups introduced are covalently bonded to the silica surface and also for PEI, with higher viscosity and lower volatility. Also, a partial degradation of TEPA might be occurring. Despite the slight decrease of CO₂ adsorption found in the first experiment, adsorption capacity after 10 cycles for this sample was still 86.3 % of the uptake achieved at the first cycle, showing a maintained but small drop after the second cycle. After 10 cycles, the CO₂ adsorption capacity for SBA-TEPA (50) sample was 9.79 % CO₂, which is still a very interesting value for post-combustion capture.

The loss in the CO₂ uptake registered for TEPA-impregnated materials along cycles has been reported previously [Xu et al., 2005; Tanthana, 2010]. However, there can also be

found studies claiming that 50 % loaded materials undergo a reduction of just 5 % in their CO₂ adsorption capacity after 40 cycles [Chuang et al., 2010].

Fig. 4. CO₂ uptake of grafted (SBA-DT (NNN)-6) and impregnated (SBA-PEI (50) and SBA-TEPA (50)) samples under streams of pure (full symbols) and diluted CO₂ (15 % vol., empty symbols) during 10 cycles. Shown uptakes are referred to the first cycle of each sample under pure CO₂.

Figure 4 also presents the cycles performed under a diluted CO₂ stream (empty symbols), the values being referred to the mass uptake during the first cycle under pure CO₂. These results point that the adsorbent with the highest nitrogen content (TEPA-impregnated sample, 15.4 %) presented a better performance in the first cycle of the series, due to their higher selectivity, as discussed in section 4.2.2. During the following adsorption cycles, DT (NNN) and PEI functionalized samples exhibited few changes in their adsorption capacities. TEPA impregnated sample underwent a slight drop in its CO₂ uptake, but its adsorption capacity after 10 cycles (8.73 % CO₂) was considerably higher than the achieved by DT (NNN) or PEI samples (4.66 and 5.47 % CO₂ respectively), due to its noticeable selectivity and nitrogen content.

3.2.4. Influence of SO₂

The influence of SO₂ in the CO₂ diluted stream was also tested, since SO₂ is typically present in the flue gas. Depending on operating conditions and the type of coal burned, SO₂ concentration in the power plant flue gas varies from 500 to 2,000 ppm [Ertl and Knözinger, 1997], with this value being limited by the European Union to 162-810 ppm SO₂ in 2001 [E.P.C., 2001]. In this work, a CO₂ diluted stream with 1,000 ppm SO₂ was used, in order to check the influence of a high SO₂ concentration. The DT (NNN) grafted sample and impregnated materials SBA-PEI (50) and SBA-TEPA (50) were selected for this study. Five adsorption-desorption cycles at 45 °C

were performed in these conditions to test the influence of SO₂ over the CO₂ adsorption performance. Figure 5b shows the mass uptake of these samples under the SO₂-containing stream (1,000 ppm SO₂) along 5 adsorption cycles, compared to the performance observed under a CO₂ diluted flow in absence of SO₂ (Figure 5a).

Fig. 5. Mass uptake of grafted and impregnated samples for CO₂ adsorption experiments at 45 °C under a) clean diluted CO₂ flow (80 % N₂, 15 % CO₂, 5 % O₂) and b) sulphur-containing CO₂ stream (85 % N₂, 15 % CO₂, 1,000 ppm SO₂).

The mass uptake when using the SO₂ containing mixture reached values of 13.86, 9.66, and 9.36 % in the first run for SBA-TEPA (50), SBA-PEI (50) and SBA-DT (6), respectively. These values correspond to an increase around 4 units in the percentage scale in their mass gain during the first cycle compared to the SO₂-free adsorption data (9.92, 5.57 and 4.82 %, for TEPA, PEI and DT (NNN) functionalized samples, respectively). Thus, it is inferred that a certain SO₂ adsorption over amino groups is taking place. Previous studies have shown that the SO₂-NH₂ reaction follows a 1:2 stoichiometry in dry conditions [Chang et al., 1995], similar to the CO₂-NH₂ reaction. This SO₂ adsorption has been observed for amino-functionalized silicas [Xu et al., 2003], and has been related to sulphate and bisulphite formation [Khatri et al., 2006], although the exact structure of the adsorbed SO₂ species has not been proposed.

During the second and successive cycles, the mass uptake experienced a steep fall when SO₂ was present, contrarily to the behaviour observed for pure or diluted CO₂. Thus, it can be considered that the NH₂-SO₂ reaction is not reversible in the regeneration conditions used (110 °C, N₂ flow), as a result of the strong bonds formed between SO₂ and amino groups previously reported [Xu et al., 2003, Khatri et al., 2006]. However, second and successive cycles still showed a certain mass gain, which can be related to the adsorption of both CO₂ (reversible) and SO₂ (non reversible). Also, SO₂ reaction with amino groups seems to be more favoured over samples with higher amino

contents. It is plausible that a high amino density promotes SO₂ adsorption as well as it does with CO₂ uptake [Aziz et al., 2012].

After the fourth cycle, mass uptake reached a plateau for all the samples. Uptake values under the “clean” and the SO₂ containing mixture at the fifth cycle are listed in Table 5. It can be seen that the reduction of the adsorption capacity in this experiment led to a common uptake value around 3-4 wt. %, which could be assigned to the remaining CO₂ adsorption capacity of the degraded materials. The formation rate of sulphate and sulphite species (related to SO₂ adsorption) has been determined to be much lower than that of CO₂ adsorption as carbonate/bicarbonate [Khatri et al., 2006]. Thus, a small CO₂ adsorption capacity remains after several adsorption cycles, while SO₂ adsorption is not maintained.

Table 5. Gas uptake at 45 °C for the fifth cycle of amine-functionalized samples under a clean mixture and a SO₂ containing stream.

3.2.5. Influence of moisture

Finally, the influence of moisture on the CO₂ adsorption capacity has been studied.

Instead of adding an excess of water into the gas mixture used, the amount used was around 5 wt. %, similar to the saturation value for water at 45 °C. CO₂ adsorption uptakes are listed in Table 6, and compared with the CO₂ uptake under dry conditions.

Although the comparison between fixed bed and thermogravimetric experiments is not straightforward, it provides some interesting information about the behavior of the materials with and without the presence of water. Figure 6 shows the breakthrough curves of CO₂ and O₂ corresponding to the analysis carried out for the sample SBA-TEPA (50). As seen, the CO₂ uptake is noticeable. On the contrary, the curves for oxygen or argon (the latter not shown here) are analogous to the obtained with the blank

analysis, so there is no real uptake of Ar or O₂ by this sample, consistently with the results of selectivity towards CO₂ shown in Section 3.2.2.

Fig. 6. Breakthrough curves of CO₂ and O₂ taken from the adsorption of SBA-TEPA (50) in a CO₂ diluted stream (80 % Ar, 15 % CO₂, 5 % O₂) with 5 % moisture.

As previously stated in Scheme 1, the CO₂/N molar ratio of the adsorption process may reach values up to 1.0 if a wet stream is used (formation of carbonate and bicarbonate), doubling the 0.5 molar ratio corresponding to the dry conditions (carbamate is formed). As a result, an increase in the CO₂ uptake is expected under a wet mixture in comparison with anhydrous conditions. However, SBA-DT (NNN)-6 sample presents a slight increment of 3.4 %. This result agrees with previous observations that have reported increments of just 10 % [Harlick and Sayari, 2007; Hiyoshi et al., 2004] and 6 % [Khatri et al., 2006], or no increment at all [Knowles et al., 2006] under wet conditions. Many experiments used much higher values of relative humidity. The CO₂ adsorption capacity increase observed for moisture contents of 27, 61 and 74 % was of 16, 22 and 60 %, respectively in aminopropyl-grafted pore-expanded MCM-41 silica [Serna-Guerrero et al., 2008]. These results were explained by the authors based on the sharp increase in water uptake at 75 % humidity. As the presence of moisture allows bicarbonate formation and considering a 1:1 stoichiometry between CO₂ and NH₂, the amount of water seems to be critical for the CO₂ uptake.

Table 6. Measured CO₂ adsorption at 45 °C of amine-functionalized samples under a gas mixture (15 % CO₂, 5 % O₂, 80 % N₂) saturated with water at 45 °C (aprox. 5 %).

Impregnated supports showed an enhancement of their adsorption capacity around 55-61 % when moisture was present in the adsorption environment. The study of other amine-impregnated adsorbents has shown an increase of 24 % [Chen, et al., 2009]. However, the differences may be due to the different impregnation conditions,

particularly the organic amount added and the mass employed in each experiment.

SBA-TEPA (50) adsorbent exhibited a slightly higher increment of the CO₂ adsorption capacity under moisture compared to PEI-impregnated material, assigned to the greater influence of chemical adsorption in the materials with higher nitrogen content, as discussed before. SBA-TEPA (50) presented a CO₂ adsorption capacity up to 16.17 % (3.7 mmol CO₂/g) under a wet diluted CO₂ stream, which is a very noteworthy value.

The cyclic behaviour of these adsorbents follows a similar trend to that discussed in dry conditions. CO₂ adsorption uptake for DT (NNN)-grafted and PEI-impregnated materials is maintained after 4 cycle, while TEPA impregnated samples shows a small but steady decrease. However, this solid presents a CO₂ uptake of 13.38 % after the fifth cycle.

Overall, fixed bed experiments have resulted in slight raise in the CO₂ adsorption capacity of grafted adsorbents and in a noticeable increase in impregnated materials, due to the presence of 5 % moisture in the inlet gas stream. Cyclic performance of the adsorbents is not modified by the presence of moisture, being completely stable for grafted and PEI-containing materials.

4. Conclusions

In this work, the adsorption of CO₂ over grafted and impregnated SBA-15 materials has been studied. Flue gas post-combustion characteristics such as dilution, cycles, sulphur and water vapour have been studied in order to test the CO₂ adsorption properties of these materials in realistic conditions.

The effect in the CO₂ uptake of a temperature increase from 25 to 200 °C was found to be different for functionalized samples. As the temperature was raised, grafted samples

(3-5 % N) showed a pronounced decreasing of CO₂ adsorption capacity, PEI impregnated material (8 % N) showed a slight decrease, and TEPA-containing sample (15 % N) underwent an increase, describing a maximum at 80 °C. The variation of the CO₂ uptake with the temperature and the selectivity towards CO₂ are both explained by the higher contribution of chemical adsorption in adsorbents with a higher nitrogen content.

The amount of CO₂ adsorbed under pure CO₂ or a diluted stream (15 % CO₂) was compared, obtaining percentage selectivity values (q_{DIL}/q_{PURE}) for these samples. This parameter was of 33 % for grafted samples and 67 and 100 % for PEI and TEPA-impregnated materials, respectively.

Grafted and PEI-containing adsorbents were stable up to 10 adsorption-desorption cycles under both pure or diluted CO₂. The TEPA-impregnated sample showed a certain decrease in its adsorption capacity due to the higher volatility of tetraethylenepentamine. However, its adsorption capacity after 10 adsorption-desorption cycles was 86 % of the initial value, which was 11.35 % CO₂ (113.5 mg CO₂/g, 2.6 mmol CO₂/g) under pure CO₂ at 45 °C.

The presence of 1,000 ppm SO₂ significantly decreased CO₂ adsorption capacity for all materials. However, a CO₂ adsorption capacity of 3-4 % CO₂ after five cycles was maintained in all cases due to the slower kinetics of the reaction of amino groups with SO₂ compared to the reaction with CO₂.

The incorporation of 5 % H₂O resulted in an increase of 3.4 % in the CO₂ uptake of DT (NNN) grafted sample. Impregnated samples underwent an increase of 50-60 % due to their higher nitrogen content and the subsequent higher relevance of chemical adsorption in these materials. SBA-TEPA (50) sample stands out, as it reached a CO₂

uptake of 16.2 % (3.7 mmol CO₂/g) in a humid stream with 15 % CO₂ at 45 °C and 1 bar.

In general, we have obtained interesting SBA-15 materials with high CO₂ adsorption capacities not affected by 10 adsorption-desorption cycles or CO₂-diluted experiments. Moreover, the presence of 5 % moisture has resulted in a CO₂ capacity increase, especially for impregnated samples. On the contrary, SO₂ has shown a negative effect in the CO₂ adsorption directly related with the amino content of the adsorbent.

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Figure Captions and Tables

Scheme 1. Reaction pathway of primary amine groups and CO₂ molecules

Fig. 1. Low angle X-Ray diffractograms for pure SBA-15 before and after functionalization by a) grafting with AP (N) and DT (NNN) or impregnation with b) TEPA and c) PEI

Fig. 2. N₂ adsorption-desorption isotherms at 77 K for pure SBA-15 and functionalized samples by a), b) grafting with AP (N) and DT (NNN) or impregnation with c), d) PEI and e), f) TEPA.

Fig. 3. Pure CO₂ uptake during temperature-programmed experiments for pure SBA-15 and samples functionalized by a) grafting with AP (N) and DT (NNN) or b) impregnation with 50 % of PEI and TEPA.

Fig. 4. CO₂ uptake of grafted (SBA-DT (NNN)-6) and impregnated (SBA-PEI (50) and SBA-TEPA (50)) samples under streams of pure (full symbols) and diluted CO₂ (15 % vol., empty symbols) during 10 cycles. Shown uptakes are referred to the first cycle of each sample under pure CO₂.

Fig. 5. Mass uptake of grafted and impregnated samples for CO₂ adsorption experiments at 45 °C under a) clean diluted CO₂ flow (80 % N₂, 15 % CO₂, 5 % O₂) and b) sulphur-containing CO₂ stream (85 % N₂, 15 % CO₂, 1,000 ppm SO₂).

Table 1. Textural properties and nitrogen content of siliceous SBA-15 and amine-functionalized samples

Adsorbent	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$D_{\text{PORE}}^{\text{b}}$ (nm)	$V_{\text{PORE}}^{\text{c}}$ (cm^3/g)	N (wt.%)
SBA-15	587	8.5	0.96	-
SBA-AP (N)-6	286	7.5	0.50	3.7
SBA-DT (NNN)-6	227	6.8	0.39	5.3
SBA-PEI (10)	399	8.8	0.79	3.4
SBA-PEI (30)	153	5.8	0.27	5.8
SBA-PEI (50)	49	-	0.09	8.3
SBA-PEI (70)	2	-	< 0.01	16.6
SBA-TEPA (10)	316	9.7	0.75	3.6
SBA-TEPA (30)	220	9.0	0.45	8.8
SBA-TEPA (50)	186	7.0	0.34	15.4
SBA-TEPA (70)	112	6.6	0.20	20.8

^a Specific surface obtained by applying the BET equation in the relative pressures range 0.05-0.2.

^b Pore diameter obtained from the maximum of the pore size distribution.

^c Total pore volume measured at a relative pressure of 0.96.

Table 2. Nitrogen content and pure CO₂ adsorption capacities at 25 and 110 °C and 1 bar for SBA-15 and amine-functionalized samples

Adsorbent	N ^a (wt. %)	q _{CO₂} ^b (wt. %)		
		25 °C	110 °C	q ₁₁₀ /q ₂₅ ^c (%)
SBA-15	-	1.42	0.12	8.3
SBA-AP (N)-6	3.7	6.18	2.05	33.2
SBA-DT (NNN)-6	5.3	7.66	2.59	33.8
SBA-PEI (50)	8.3	7.58	5.10	67.3
SBA-TEPA (50)	15.4	9.77	8.19	83.8

^a Organic content measured by elemental analysis.

^b CO₂ adsorption capacity measured by thermogravimetry at the shown temperature.

^c CO₂ adsorption uptake at 110 °C compared to the value achieved at 25 °C.

Table 3. Degasification temperature and CO₂ adsorption capacity achieved at 45 °C and 1 bar for SBA-TEPA (50) impregnated sample

Adsorbent	T ^a (°C)	q _{CO₂} ^b (wt. %)
SBA-TEPA (50)	60; 3 h	10.19
	80; 3 h	10.92
	90; 3 h	11.11
	100; 3 h	11.35
	110; 3 h	8.95
	110; 6 h	5.48

^a Degasification conditions (temperature and time) employed under 100 mL/min N₂.

^b CO₂ adsorption capacity measured by thermogravimetry at 45 °C.

Table 4. Gas uptake at 45 °C with pure and diluted CO₂ of amine-functionalized samples

Adsorbent	N ^a (% w.)	q (wt.%)		
		Pure ^b	Diluted ^c	q _{DIL} /q _{PURE} ^d (%)
SBA-15	-	0.75	0.17	22
SBA-AP (N)-6	3.7	4.68	3.78	81
SBA-DT (NNN)-6	5.3	6.69	4.82	72
SBA-PEI (10)	3.4	2.07	1.04	50
SBA-PEI (30)	5.8	2.80	1.95	69
SBA-PEI (50)	8.3	7.49	5.57	74
SBA-PEI (70)	16.6	9.80	9.00	92
SBA-TEPA (10)	3.6	1.98	0.93	47
SBA-TEPA (30)	8.9	7.04	5.56	79
SBA-TEPA (50)	15.4	11.35	10.04	89
SBA-TEPA (70)	20.8	11.06	11.47	103

^a Organic content measured by elemental analysis.

^b CO₂ adsorption capacity measured by thermogravimetry with a pure CO₂ flux of 100 mL/min.

^c CO₂, N₂ and O₂ combined adsorption capacity measured by thermogravimetry with a mixed flux (80 % N₂, 15 % CO₂, 5 % O₂) of 100 mL/min.

^d CO₂ adsorption capacity under a diluted CO₂ stream (80 % N₂, 15 % CO₂, 5 % O₂) referred to the value obtain under pure CO₂.

Table 5. Gas uptake at 45 °C for the fifth cycle of amine-functionalized samples under a clean mixture and a SO₂ containing stream.

Adsorbent	N ^a (% w.)	q ^b (wt.%)		
		Clean Mix	SO ₂	Δq ^c (%)
SBA-DT (NNN)-6	5.3	4.74	3.94	-17
SBA-PEI (50)	8.3	5.53	4.30	-22
SBA-TEPA (50)	15.4	9.10	3.53	-61

^a Organic content measured by elemental analysis.

^b Mass uptakes corresponding to the fifth adsorption cycle of each series.

^c Decrease of the CO₂ uptake between adsorption with a diluted CO₂ stream and a similar mixture containing 1,000 ppm SO₂.

Table 6. Measured CO₂ adsorption at 45 °C of amine-functionalized samples under a gas mixture (15 % CO₂, 5 % O₂, 80 % Ar) saturated with water at 45 °C (aprox. 5 %).

Sample	N ^a (wt. %)	CO ₂ ^b (wt. %)	CO ₂ ^c (wt. %)				Δq ^d (%)
			Cycle 1	Cycle 2	Cycle 3	Cycle 4	
SBA-DT (NNN)-6	5.3	4.82	4.99	4.93	4.56	4.56	3.4
SBA-PEI (50)	8.3	5.57	8.61	8.48	8.12	8.10	55
SBA-TEPA (50)	15.4	10.04	16.17	15.55	14.50	13.38	61

^a Organic content measured by elemental analysis.

^b Mass uptake measured by thermogravimetry with a mixed flux (80 % N₂, 15 % CO₂, 5 % O₂) of 100 mL/min.

^c CO₂ adsorption capacity in a fixed bed under a diluted CO₂ stream (80 % Ar, 15 % CO₂, 5 % O₂, dry conditions) with 5 wt. % water.

^d Increase in CO₂ adsorption capacity when using the gas mixture with 5 % water compared to anhydrous adsorption with fresh sample.