

1. PROBLEM ADDRESSED

The exponential growth of the anthropogenic greenhouse gas emissions in the last 150 years has led to a global warming and to the well-known climate change. One of the main goals of the international community for the XXI century is to reduce these emissions, especially of CO₂, with the aim of limiting the global temperature increase to 2 °C above the pre-industrial value [1]. Thus, the combination of energy saving and efficiency with a large-scale use of renewable energy is essential. In addition, carbon capture and storage (CAC) from large stationary sources has been highlighted as a key technology to accomplish this objective [2].

2. SUMMARY AND KEY INNOVATIONS

The present study started as a collaboration contract between the *Universidad Rey Juan Carlos* and *ENDESA S.A.*, one of the main electric power companies in Spain, through a 4-year CENIT project (National Strategic Consortium for Technical Research).

This investigation addresses the synthesis of siliceous mesostructured materials and their modification with amino-containing molecules. The main objective is to obtain solid sorbents which are highly selective towards CO₂, so that they can be used as CO₂ adsorbents in high stationary sources such as thermal power plants. A wide variety of mesostructured materials with different textural properties has been prepared. Then, co-condensation, grafting and impregnation techniques have been used for the incorporation of functional groups in the siliceous supports.

Relevant conclusions have been drawn regarding the preparation, characterisation and use of these materials. The main points are the following:

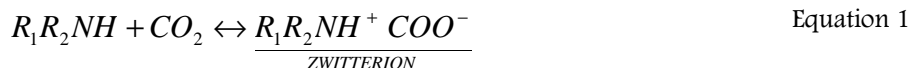
- The drying step of amino-functionalized solids was thoroughly studied, finding a slow degradation reaction under widely-used drying conditions. As a result of this research, it was stated that the heating of these materials (drying, degasification or regeneration steps) must be performed with the absence of air in order to avoid the undesired reaction of amino groups.
- The location of amino groups incorporated by each functionalization technique was also examined by the combination of transmission electron microscopy (TEM) with a staining technique. As a result, a clear correlation was found between the functionalization route employed and the efficiency of the amino groups in CO₂ adsorption. Briefly, the grafting technique favours a high incorporation of amino groups, which are located on the silica surface, being accessible by CO₂ molecules. Contrarily, the co-condensation route, carried out under highly acidic conditions, leads to the protonation of amino groups and their embedding inside the silica walls, thus hindering further reactions with CO₂. Finally, the impregnation of polymeric (PEI, polyethyleneimine) or linear compounds (TEPA, tetraethylenepentamine) resulted in different dispersions throughout the porous structure, with their accessibility being also dissimilar. The TEPA molecule yielded the best dispersion and increasing adsorption efficiencies for higher organic loadings.
- In addition, a novel functionalization path was developed for the incorporation of amino groups, consisting in the impregnation of materials previously functionalized by grafting. This technique, called “double functionalization”, yielded significant adsorption capacities, as high as 235 mg CO₂/g ads at 45 °C and 1 bar, with adsorption efficiencies of 0.45 mol CO₂/mol N, very close to the theoretical maximum of 0.50 mol CO₂/mol N. These results are among the highest values found in the literature to date and were ascribed to a synergy between the amino groups incorporated by each functionalization technique. Namely, the presence of mobile amino groups favours the second step of the CO₂-NH₂ reaction mechanism, i.e. the charge rearrangement between an amino group and a zwitterion formed by CO₂ and a fixed amino group. In this step the proximity of both species is a key variable and is promoted by the combined presence of fixed and mobile amino moieties.
- Finally, the CO₂ adsorption properties of these adsorbents were tested using conditions of temperature, pressure and composition similar to those present in industrial post-combustion

facilities. CO₂ was diluted to 15 %, a moisture content of 5 % was used and impurities such as 1000 ppm SO₂ were considered. In addition, the agglomeration process and the cyclic behaviour in up to 10 adsorption-desorption tests were evaluated. Summarily, the prepared adsorbents showed an excellent behaviour under real conditions, a fact that qualifies them for their use in industry.

3. STATE OF THE ART

The first works devoted to CO₂ capture with solid sorbents go back to the '90s, addressing the research on obtaining CO₂ sorbents to replace the current lithium hydroxides, with high CO₂ uptakes (300 mg CO₂/g ads) but no regenerability. Several attempts by the *Hamilton Sunstrand Space Systems International* resulted in HSC⁺ materials, consisting of polyethyleneimine (PEI) supported over polymethylmethacrylate monoliths, with high selectivity towards CO₂ even at pressures as low as 1 Torr (1.33 mbar) [3, 4].

The reaction mechanism between CO₂ and primary or secondary amines is schematised in Equations 1 and 2. As seen, the first step involves the formation of a zwitterion by the combination of CO₂ and one amino group. The second step requires a basic group that stabilises the charge of the zwitterion. In anhydrous conditions, amino groups are the only basic groups available.



After the good results of polyethyleneimine, the group of Prof. Song at Pennsylvania State University developed the so-called *molecular basquet*, impregnating PEI in the porous structure of MCM-41 [5, 6]. The optimum ratio PEI/MCM-41 was found to be of 50 %, yielding adsorption capacities of 44 and 112 mg CO₂/g ads at 50 °C and 75 °C respectively (pure CO₂, 1 atm). These values exceeded those corresponding to PEI or MCM-41 by themselves, so it was stated that the incorporation of PEI in the porous structure of MCM-41 led to a synergic effect. The increase of the adsorption capacity with the temperature was assigned to kinetic factors and thus to a better CO₂ diffusion, a fact that was confirmed later on. However, there is another unverified claim regarding a change in the PEI packing inside the pores with the temperature.

Several modifications of the adsorbents, such as the use of Al-MCM-41 or the addition of polyethylene glycol, produced an increase in the CO₂ uptake, as well as faster adsorption and desorption kinetics for the latter [6]. Al-MCM-41-PEI-50 sorbent reached an adsorption capacity of 127 mg CO₂/g ads at 75 °C and 1 atm of pure CO₂. As a result of these early studies, the number of papers using PEI for CO₂ capture rose significantly. For example, the selectivity of this polymer towards CO₂ in the presence of O₂ and N₂ was evaluated [7, 8, 9, 10]. The use of PEI was extended to other porous materials, such as MCM-48, SBA-15, SBA-16 and KIT-6 [11, 12] and other supports such as fiberglass [13] and monoliths [14]. Moreover, the chemical features of PEI made it useful for the capture of other acidic gases, such as H₂S [15, 16, 17].

The advance in research in 2004 led to the use of a diluted CO₂ stream (14.9 %) that allowed the estimation of CO₂/O₂ and CO₂/N₂ selectivity in 180 and 1,000 times [7]. Despite this positive finding, the CO₂ uptake under diluted CO₂ was only of 88 mg CO₂/g ads (75 °C), a reduction of 20 % compared to the value under pure CO₂. However, the use of a diluted CO₂ stream saturated with water (75 °C, 12.6 % moisture) yielded an adsorption capacity of 130 mg CO₂/g ads, thus corroborating the positive effect of water vapour in the adsorption of CO₂ with amino groups [18]. The stability of weak structures such as MCM-41 also seemed to be improved by the pore filling with PEI [9], although only 10 cycles were applied, which might be insufficient to guarantee the stability of the impregnated support in the long term.

The grafting of organosilanes was also developed in the '90s, when in 1995 C. Ovalles and his co-workers from *INTEVEP* and the *Universidad Central de Venezuela* reported the preparation of an amorphous silica gel grafted with aminopropyl-trimethoxysilane, AP (N), with one amino group. The nitrogen content incorporated was only of 1.8 %, thus leading to low CO₂ uptake: 8.1 and 15.1 mg CO₂/g ads at 23 °C and 50 °C respectively [19]. Despite that result, the grafting of amino-containing organosilanes was recognised as an interesting technique to produce CO₂ sorbents.

In 2002 the group of Prof. Chaffee in *Monash University* (Australia) used the grafting procedure to modify HMS porous silica with diethylenetriaminopropyl-trimethoxysilane, DT (NNN), a molecule with three amino groups [20]. The nitrogen content incorporated was of 6.4 %, reaching a CO₂ uptake of 82 mg CO₂/g ads (20 °C, 1 atm pure CO₂).

This outcome boosted the interest in amino-modified materials as CO₂ sorbents in the following years. Infrared spectroscopy was used to determine the heat of adsorption by Prof. Soong in *The University of Akron* and the *National Energy Technology Laboratory*, from the Department of Energy of the US [21]. The grafting technique was also employed to functionalize other materials, such as SBA-15 [22] and MCM-48 [23], leading to interesting results and adsorption capacities around 90 mg CO₂/g ads (20 °C, 1 atm pure CO₂). It was also determined that grafted AP (N) molecules were stable up to 200 °C and that the CO₂ adsorption was reversible, with regeneration of the solids being possible by heating them up to 75 °C in a He flux. In addition, they claimed a duplication of the CO₂ uptake in the presence of moisture. However, such a large increase is questioned, since later studies have registered small increments around 6-10 % [24, 25] or even no increment at all [26, 27] with similar materials.

In 2005 and 2006 the research group of A.L. Chaffee studied the features of CO₂ adsorption over HMS and commercial silicas grafted with aminopropyl, AP (N), ethylenediamine, ED (NN) [28], and diethylenetriamine, DT (NNN) [26]. Samples with AP (N) and ED (NN) were found to be more efficient than those with DT (NNN).

The use of tetraethylenepentamine (TEPA) is more recent, since its utilisation for impregnation started in 2006, when the group of Prof. Cao in *Nanjing University* (China) incorporated it over SBA-15 [29]. The incorporation of 50 % TEPA over uncalcined SBA-15 yielded an adsorption uptake of 106 mg CO₂/g ads at 45 °C and 1 atm, this value rising up to 144 and 155 mg CO₂/g ads when increasing the temperature to 75 °C and 100 °C, respectively. Furthermore, increasing the amount of TEPA impregnated to 70 % resulted in the maximum adsorption capacity of 173 mg CO₂/g ads. This group also determined the adsorption kinetics of TEPA-containing sorbents, finding a fast process that only took 2 minutes to adsorb 75 % of its equilibrium adsorption capacity. However, more than 2 h were necessary to reach the equilibrium. Thus, it was stated that the CO₂ adsorption process in these kinds of materials is controlled by kinetic factors; namely, the CO₂ diffusion to the active amino groups.

Some other studies continued the research line of TEPA, impregnating siliceous materials such as MCM-41 or silica monoliths [14], showing promising results. Nevertheless, the cyclic behaviour of these sorbents in repeated adsorption-desorption cycles exhibited a certain decrease in the adsorption capacity originated by the loss of organic compound in the regeneration steps [30].

As observed, the use of adsorption temperatures of 25 °C is common for adsorption analysis with grafted samples, while impregnated samples are usually tested at 75 °C or higher temperatures. The objective is to work at the optimum conditions for each material, looking for the maximum CO₂ adsorption uptake, which depends on the nature of the incorporated compound. In the present PhD dissertation a temperature of 45 °C has been used systematically, regardless of the kind of material tested. This value was selected due to its practical industrial interest, since the gas fumes in a typical coal-fired thermal power station are released at 45 °C after the desulphurization unit [31].

4. APPLICATIONS, IMPLEMENTATIONS AND RESULTS

The main findings of the present PhD dissertation are summarised below:

1. More than 20 silica-based **mesostructured materials** were synthesised, with SBA-15 being the reference material due to its high pore diameter (9 nm) and pore volume (1.03 cm³/g). Furthermore, the synthesis procedure of SBA-15 was modified in order to obtain additional advantages. Thus, aluminium was incorporated to Al-SBA-15 materials, with the aim of improving CO₂ adsorption in the presence of moisture. In addition to this, numerous pore-expanded SBA-15 supports were prepared, with SBA-PE-17e standing out among them due to its large pore diameter of 15.2 nm and its high pore volume (1.18 cm³/g). The latter provides enough space for the incorporation of aminated molecules while the noticeable mean pore diameter allows a rapid diffusion of organic molecules and CO₂.

Additionally, several series of HMS supports with pore diameters ranging from 1.4 to 2.8 nm were synthesised in order to test the influence of this variable in the adsorption of CO₂. A commercial Silica Gel was also used to compare the results of a commercially available support with those of the abovementioned synthesised sorbents.

The N₂ adsorption-desorption isotherms of some selected samples are presented in Figure 1, where their different structures are shown. As previously stated, the textural properties of SBA-PE-17e are very interesting.

However, these samples present a CO₂ uptake between 10.4 and 22.3 mg CO₂/g ads at real industrial conditions (45 °C, 1atm). In order to increase their CO₂ adsorption capacity, these supports can be modified by incorporating amino groups into their porous structures.

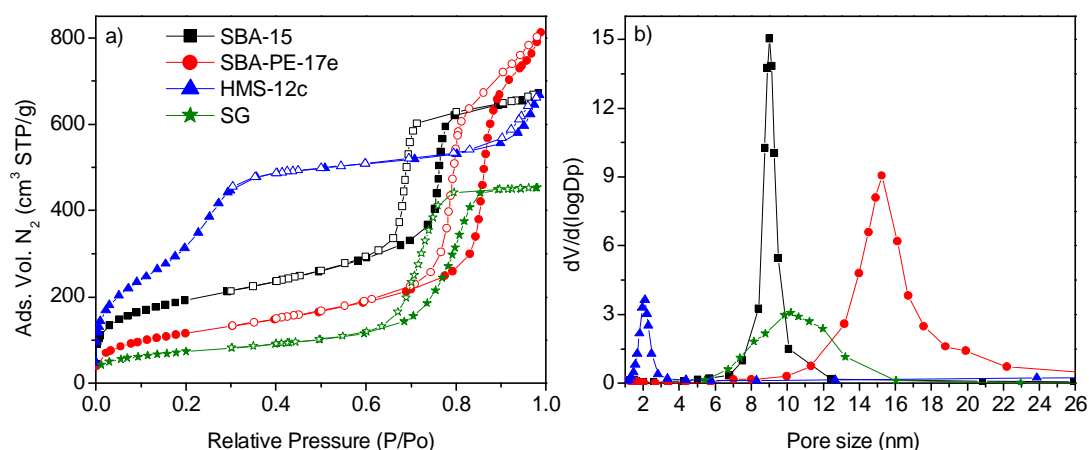


Figure 1. Characterisation of SBA-15, SBA-PE-17e, HMS-12c and SG siliceous supports: a) N₂ adsorption-desorption isotherms at 77 K and b) BJH pore size distributions.

2. Firstly, silica supports were modified by **grafting** with organosilanes containing one, AP (N), two, ED (NN), and three, DT (NNN), amino groups. This technique yields covalent bonds between the silica surface and the organic molecules used. A nitrogen incorporation of up to 8.4 % was reached with DT (NNN), close to the maximum of 8.6 % obtained in the literature in similar conditions, although a modified method yielded nitrogen contents of up to 11.2 % [25].

As observed in Figure 2, the CO₂ isotherm of SBA-15 siliceous support is characteristic of physical adsorption. On the contrary, isotherms corresponding to amino-containing samples present features derived from the existence of chemical adsorption. The differences between these two groups can be assigned to the chemisorption of CO₂ over amino groups.

Amino groups presented a high efficiency in CO₂ capture, ranging from 0.30 to 0.37 mol CO₂/mol N, except for samples containing AP (N), where the contribution of physical adsorption was significant and this parameter exceeded the maximum theoretical

value for chemisorption, 0.50 mol CO₂/mol N (due to the 1:2 stoichiometry between CO₂ and amino groups).

Capture efficiency increased with the surface density of organosilanes tethered and with the reduction of the chain length of organosilanes. However, due to the higher nitrogen content of diethylene-trimethoxysilane, DT (NNN), the best results were observed for SBA-DT (NNN)-6 sample. A CO₂ adsorption capacity of 82 mg CO₂/g ads was reached with an efficiency of 0.36 mol CO₂/mol N (45 °C, 1 bar).

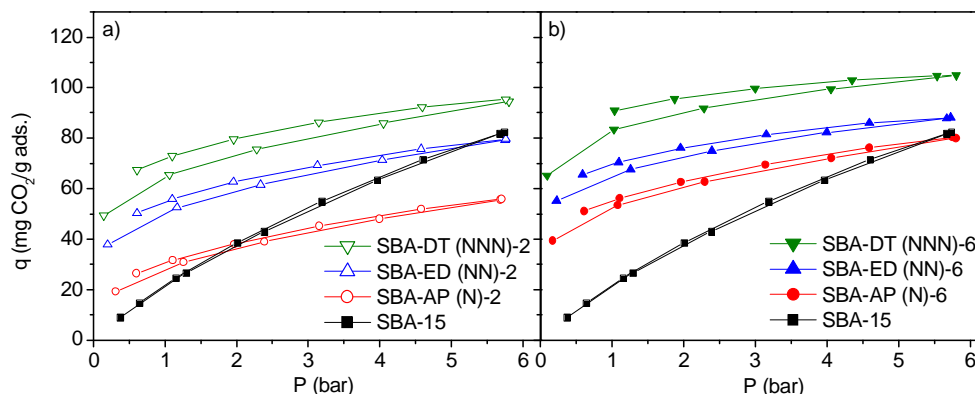


Figure 2. CO₂ adsorption-desorption isotherms at 45 °C of SBA-15 silica functionalized by grafting with AP (N), ED (NN) y DT (NNN) assuming a) 2 SiOH/nm² and b) 6 SiOH/nm².

After the functionalization with DT (NNN)-6 of all prepared supports, SBA-15 and SBA-PE-17e obtained the best results both in terms of CO₂ uptake and adsorption efficiency. The explanation lies in their open porous structures and large pore volumes. Additionally, organosilanes with tertiary amino groups or else without amino groups were tested. From the CO₂ adsorption results it was verified that tertiary amino groups do adsorb CO₂ in the presence of moisture but not in anhydrous conditions.

3. The drying step of grafted materials was found to be very relevant. A heating at only 110 °C in air caused a significant drop in the CO₂ uptake of ED (NN) and DT (NNN)-grafted samples, as shown in Figure 3. This effect was ascribed to a slow degradation of the secondary amino groups present in ED (NN) and DT (NNN), resulting in C=N and C=O-N functionalities, which do not react with CO₂. Since AP (N) contains only one primary amino group it is coherent that its CO₂ uptake is not altered after the drying step. A similar drying treatment was performed under vacuum, finding no negative effects in the amino groups and allowing several adsorption-desorption cycles to be carried out with a constant CO₂ adsorption capacity. These findings are even more significant when the materials are used at industrial scale, where reutilisation is essential.

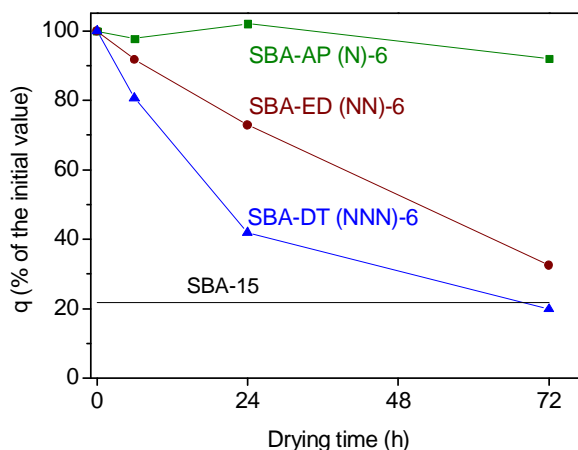


Figure 3. Dependence of the CO₂ uptake with the drying time (110 °C, air) for AP (N), ED (NN) and DT (NNN)-grafted SBA-15 materials.

Before the publication of this study, it was usual to find publications claiming that ethylenediamino moieties, ED (NN), tethered over silica supports, were stable in air up to 200-250 °C [32, 33]. These common mistakes arose from the use of dynamic analyses to determine the stability of samples, often employing fast heating rates of 5-10 °C/min, so that the slow degradation process at 110 °C was missed.

4. A co-condensation method was also applied to incorporate AP (N), ED (NN), and DT (NNN) over SBA-15. Low nitrogen contents were incorporated by these samples (between 1.3 and 2.7 %), which also presented low CO₂ uptakes (from 10.1 to 11.2 mg CO₂/g ads). This fact originates from the highly acidic medium employed (1.9 M HCl solution), where amino groups are protonated. In this situation, amino moieties crosslink with the silica precursor and end up embedded inside the silica walls, out of the reach of CO₂ molecules.

5. The impregnation procedure consists of the filling of pores and no chemical reaction is produced. Then, any organic molecule can be used and also higher organic incorporations are achieved. However, the efficiency in CO₂ capture is lower than that obtained by grafting, as amino groups are not so easily reachable by CO₂ molecules. A series of organic compounds with primary, secondary and tertiary amino groups in aliphatic or aromatic chains was used. It was found that amino groups substituted in aromatic rings or close to them do not react with CO₂ because their unpaired electrons are delocalised in the electron cloud of the aromatic ring (molecule of pyrimidine). Also, some molecules, such as hexamethylamine, do not provide enough nitrogen to the material to achieve a considerable CO₂ uptake. Also, some light compounds, such as ethylenediamine or piperazine, presented respectively large losses by evaporation in the pre-degasification step and during the cycles. Polyethyleneimine (PEI) and tetraethylenepentamine (TEPA) molecules were selected to perform further studies as a result of their efficiency and stability:

a. The impregnation of PEI over SBA-15 resulted in the incorporation of nitrogen contents up to 16.6 %. Besides, CO₂ capture efficiencies were in the range of 0.27 to 0.18 mol CO₂/mol N, decreasing with the organic amount incorporated due to the polymeric nature of PEI. However, the use of pore-expanded materials yielded sorbents with higher capacities and efficiencies due to the better dispersion of PEI along the surface. Thus, efficiencies up to 0.33 mol CO₂/mol N were observed. A maximum CO₂ uptake of 138 mg CO₂/g ads was obtained (45 °C, 1 bar), corresponding to SBA-PE-17 e-PEI (50) sample.

b. TEPA-containing SBA-15 yield nitrogen contents up to 20.8 %. CO₂ efficiencies are around 0.20 mol CO₂/mol N. Contrary to PEI, this parameter is maintained or even increased with higher organic contents, since TEPA is better dispersed. The use of pore-expanded SBA-15 also resulted in higher efficiencies, up to 0.37 mol CO₂/mol N. The best adsorption capacity was 198 mg CO₂/g ads, observed for SBA-PE-17 e-TEPA (50) sample (45 °C, 1 bar).

6. A new double functionalization technique was developed during this research. It consists of the impregnation of samples previously functionalized by grafting. AP (N) and DT (NNN) moieties were used for the grafting step, while the PEI and TEPA were employed for the impregnation of grafted samples. The reaction mechanism between CO₂ and amino groups has two steps (see Equations 1 and 2). The double functionalization technique, i.e. having mobile and fixed amino groups at the same time, aims to promote the second step, in which the proximity of two amino groups is crucial.

Higher organic contents were obtained in comparison with impregnated samples. Also, double-functionalized materials exhibited the highest efficiencies in CO₂ capture, as a result of the better contact between fixed and mobile amino groups and the enhanced dispersion and mobility of impregnated molecules. The AP (N)-6-TEPA (50) sample reached an outstanding value of CO₂ adsorption capacity, 215 mg CO₂/g ads, with an efficiency of 0.45 mol CO₂/mol N (45 °C, 1 bar), very close to the theoretical maximum of 0.50 mol CO₂/mol N.

A schematic diagram of the amino group disposition obtained by grafting, impregnation and double functionalization is depicted in Figure 4.

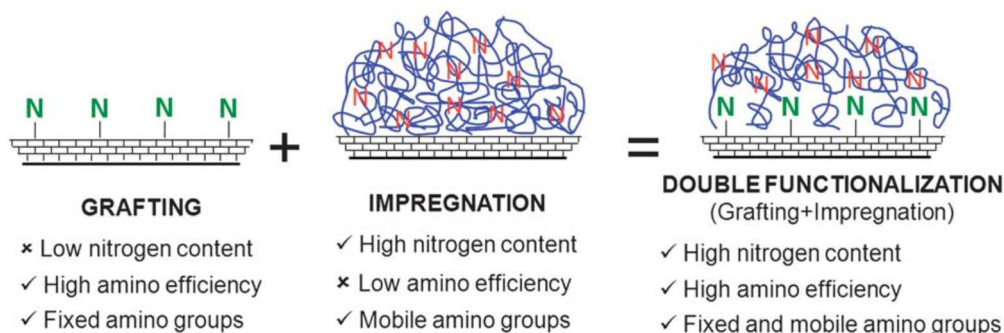


Figure 4. Schematic drawing of the grafting, impregnation and double functionalization processes and a summary of their advantages and drawbacks.

The **location of amino groups** has been determined by a procedure consisting of the combination of Transmission Electron Microscopy (TEM) and a staining technique. The staining agent, RuO_4 , oxidises the amino groups, being then deposited over them as RuO_2 . As a result, the electron density around amino groups is increased and they become visible by TEM (otherwise they are not detectable due to their low molecular weight). The different locations of amino groups found for samples functionalized by grafting, co-condensation and impregnation explained their CO_2 adsorption behaviour, as summarised below.

The use of this technique allowed the determination that amino groups incorporated by co-condensation were homogeneously scattered, not only over the silica surface, but also embedded inside the silica walls. This arrangement, together with the protonation of amino groups during the synthesis, explains the low efficiency in CO_2 capture of these functionalities. Micrographs of grafted materials clearly revealed the disposition of amino groups inside the pores, thus being completely accessible to CO_2 and resulting in high adsorption efficiencies. The increase of the organic loading produced an evolution of the isolated groups of RuO_2 to a complete pore filling.

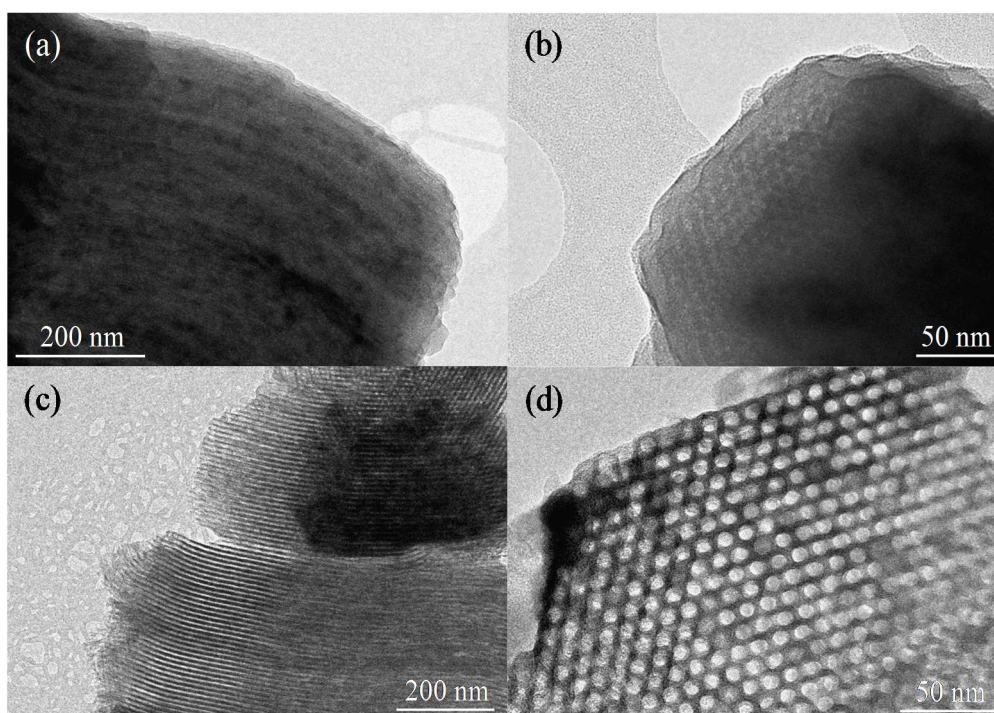


Figure 5. Transmission electron micrographs for SBA-TEPA (30) sample a), b) stained with RuO_4 and c), d) not stained.

Finally, impregnated samples showed a dissimilar behaviour. On one hand, TEPA-containing samples presented an appropriate organic diffusion inside the pores. These materials obtained a steady CO₂ adsorption efficiency when the amount of TEPA was increased. Thus, it can be concluded that the diffusion of CO₂ through a layer of TEPA is not hindered by an increase in the organic amount. Some of the images are shown in Figure 5, where stained samples (Figures 5a and 5b) clearly reveal pores filled with amino groups. In contrast, if the sample is not stained with RuO₄, TEPA is not visible (Figures 5c and 5d).

On the other hand, TEM micrographs of PEI-impregnated materials suggest that a significant part of the polymer is not incorporated inside the porous structure, remaining in the external surface. This fact is ascribed to the high viscosity of PEI, which hinders its access to the pores. However, the hypothesis of PEI completely diffusing inside the pores but RuO₄ not being able to reach deep amino groups is also plausible. In both cases, this arrangement explains the decreasing adsorption efficiency of PEI-impregnated samples when the organic loading is increased.

7. Several relevant parameters in the **industrial CO₂ adsorption** process were studied, such as CO₂ dilution, cyclic reutilisation and the presence of impurities and moisture.

a. The CO₂ adsorption capacity of materials in **diluted CO₂** (15 %) and pure CO₂ streams was compared. A q_{DIL}/q_{PURE} ratio of 20 % was obtained by siliceous SBA-15. In this material, physical adsorption is the only mechanism taking place and the CO₂ partial pressure determines the mass uptake. On the contrary, values of 70-80 % for q_{DIL}/q_{PURE} were found for grafted samples and up to 90 % and 100 % for materials impregnated with PEI and TEPA respectively. This trend is directly related to the nitrogen content of the adsorbents and the accessibility of their amino groups, being a measure of the contribution of chemisorption to the adsorption of CO₂.

b. The presence of **1,000 ppm SO₂** in the gas mixture resulted in a significant decrease in the CO₂ adsorption capacity of functionalized samples due to the selective irreversible reaction between SO₂ and amino groups. The adsorption capacity decreased along five adsorption-desorption cycles and a remaining CO₂ uptake was found due to the difference in CO₂ and SO₂ adsorption kinetics. However, at the fifth cycle, mass uptake was reduced in 17 %, 22 % and 60 % (compared to the values without SO₂) for samples functionalized with DT (NNN), PEI and TEPA respectively. This drop was found to depend on the nitrogen content of the adsorbents, so that it was higher for TEPA-containing samples.

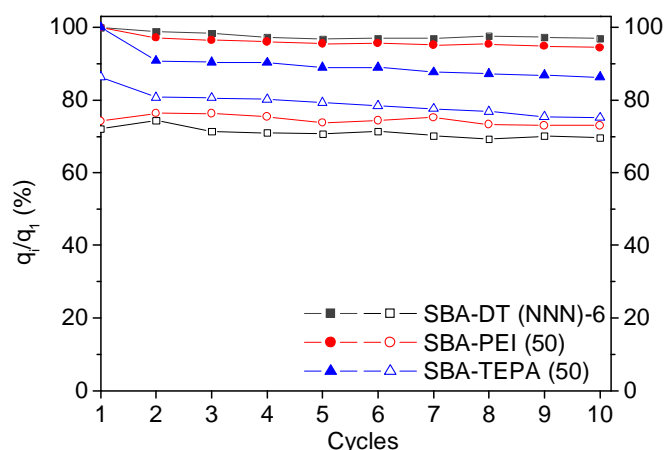


Figure 6. CO₂ uptake of amino-functionalized samples under streams of pure (full symbols) and diluted CO₂ (15 % vol., empty symbols) during 10 cycles. Shown uptakes are referred to the first cycle of each sample under pure CO₂.

c. Adsorbents prepared by grafting with DT (NNN) or impregnation with PEI are stable after 10 **adsorption-desorption cycles** (see Figure 6). In these conditions, TEPA-containing materials suffer a slight but constant loss of adsorption capacity due to the partial evaporation and possible degradation of this compound. However, the TEPA-impregnated sample achieved

the highest CO₂ adsorption capacity after 10 cycles in diluted CO₂ due to its high organic content and the preponderance of chemical adsorption in this material.

d. The presence of **5 % moisture** in the feed gas results in a general increase of CO₂ adsorption capacity, up to 40 % and 70 % for impregnated materials. As a result, sample AP (N)-6-TEPA (50) achieves a noticeable adsorption capacity of **235 mg CO₂/g ads** (0.15 bar CO₂, 45 °C). Cyclic experiments in a wet stream showed a maintained capacity for DT (NNN) and PEI-containing adsorbents, while samples with TEPA experienced a continuous loss in the CO₂ uptake.

e. Since all the supports and functionalized samples synthesised are powders, their **agglomeration** is critical for their industrial use in a fixed bed. The conventional agglomeration process was performed with bentonite and methylcellulose as inorganic and organic binders respectively. Two unconventional methods were also implemented in order to avoid the calcination of the pellets obtained: the substitution of methylcellulose for an amino-containing organic binder and alternatively, the use of microwave radiation without the use of any organic binder. All extruded materials reached an acceptable hardness. Besides, the use of microwave radiation allowed the formation of bonds between SBA-15 and bentonite, avoiding the calcination step. As a consequence, amino-functionalized materials could be agglomerated, preserving the organic functionalities.

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