

Amino functionalized mesostructured SBA-15 silica for CO₂ capture: Exploring the relation between the adsorption capacity and the distribution of amino groups by TEM

Raúl Sanz^{1*}, Guillermo Calleja¹, Amaya Arencibia¹ and Eloy S. Sanz-Pérez²

¹Department of Chemical and Energy Technology,

²Department of Chemical and Environmental Technology

School of Experimental Sciences and Technology (ESCET)

Rey Juan Carlos University, c/ Tulipán s/n, E-28933 Móstoles, Madrid, Spain

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*To whom correspondence should be addressed

Phone: 34 91 488 80 93

Fax: 34 91 488 70 68

E-mail: raul.sanz@urjc.es

Abstract

The distribution of amino groups on amino-functionalized SBA-15 materials for CO₂ adsorption was studied by Transmission Electron Microscopy (TEM) in combination with a staining technique using RuO₄ in order to analyse the influence of the aminated organic chains location on the CO₂ adsorption properties. Mesostructured amino-functionalized SBA-15 materials were obtained by co-condensation, grafting and impregnation using aminopropyl, AP (N), ethylene-diamine, ED (NN), diethylene-triamine, DT (NNN) and polyethyleneimine, PEI, as functionalizing agents. CO₂ adsorption isotherms of functionalized samples at 45 °C showed that both the adsorption capacity (mg CO₂/g ads) and the efficiency of amino groups (mol CO₂/mol N) depend on the functionalization technique and the amount of organic compound used. While samples synthesized by co-condensation showed negligible CO₂ uptake and efficiency, adsorbents prepared by grafting and impregnation presented significant CO₂ adsorption capacities but a dissimilar efficiency. Key differences in the location of aminated chains explained the performance of CO₂ capture for every adsorbent, being grafted samples the adsorbents where amino groups were better distributed, favouring the CO₂ diffusion through the whole structure.

Keywords: Mesostructured silica, amino-functionalized SBA-15, staining technique, transmission electron microscopy, CO₂ adsorption.

1. Introduction

Global warming is considered to be caused by the anthropogenic emissions of greenhouse gases (GHG). Carbon dioxide, which mainly comes from fossil fuel combustion, is the most important source representing a 72 % of the total GHG emissions¹. To face this problem Carbon Capture and Storage (CCS) techniques are being proposed as feasible technologies to effectively minimise CO₂ emissions^{2,3}.

The commercially available techniques for CO₂ capture are based on absorption with liquid amine compounds such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). However, these absorption processes present as disadvantages the liquid mixture corrosivity, the amine waste during operation, and the high energy cost of the regeneration process^{4,5}.

Consequently in the last years there has been an increasing interest in developing efficient selective adsorbents for CO₂ capture as an alternative to liquid absorption.

Thereby, zeolites, activated carbons, mesostructured silicas, and metal-organic frameworks have been investigated for the removal of carbon dioxide⁶. Among these solid supports, mesostructured inorganic silica materials such as M41S, HMS, MSU and SBA families⁷⁻¹², stand out due to their high surface area and pore volume, as well as their uniform mesopore size.

For CO₂ removal, mesostructured supports are functionalized with organic molecules containing basic amino groups, which act as specific sites for CO₂ capture by chemical adsorption¹³⁻¹⁹. The incorporation of functional groups can be achieved by different methods based on either chemical or physical surface modification. The chemical procedure is based on the use of organosilane molecules containing several amino

groups as amino precursors^{13,14}, and can be accomplished by two routes: the grafting method, which is based on the reaction between an organoalcoxysilane precursor of the organic chain and the silanol groups of the previously obtained silica support, and the co-condensation method, that involves the simultaneous condensation in the synthesis medium of the organoalcoxysilane compound and the alcoxysilane precursor of the silica structure^{20,21}. The physical modification consists on the incorporation of organic molecules or polymers that contain many amino groups, such as polyethyleneimine (PEI)¹⁵⁻¹⁷ or alike^{18,19} to the silica support. The PEI compound is a polymer with a large number of amino sites and can be incorporated to the silica by impregnation into the channels of mesoporous sieves^{15,16} or by acid-catalysed hyperbranching surface polymerization¹⁷. In general, PEI functionalized materials exhibit a surface concentration of amino groups on the mesopore walls much higher than other materials obtained by silanization with organoalcoxysilanes.

One of the most important problems related to the characterization of these amino containing mesostructured materials, regardless of the method followed to obtain them, as well as other hybrid organic-inorganic mesoporous structures, is to find out the resulting distribution of amino groups on the material structure, which can be located either coating the outer surface of the particles or homogeneously distributed within the pores, or even blocking the pores entrance. Usually, the location and accessibility of the incorporated functional groups are not determined²¹.

Some work related to hybrid organic-inorganic mesostructures has been published, focused on indirect methods to establish the possible location of the organic functional groups. Stein et al. compared the properties of vinyl-functionalized MCM-41 silica obtained by grafting and co-condensation in one of the early reports of functionalization²². Based on nitrogen adsorption experiments, XPS, and a kinetic study

of the bromination reaction with vinyl groups, it was thoroughly argued how the distribution of the organic groups was. XPS coupled with argon etching of the surface of MCM-41 grafted with a copper complex was also used to explore the distribution of the transition complex within the pores and the external surface²³. Other indirect assessment of the location of organic groups has been the analysis of the accessibility of functional groups for the adsorption of heavy metals on the surface of functionalized materials, such as mercury on thiol groups²⁴⁻²⁷. In fact, since the mercury uptake was related to the sulphur content, relevant conclusions were extracted about the stoichiometry of the interaction and accessibility of functional groups^{25,26}. Some reports have also described the distribution of amino groups in amino functionalized mesostructured solids. Yokoi et al. studied MCM-41 samples functionalized with mono, di and triamino-organosilanes obtained by grafting and co-condensation in order to elucidate if the organic groups were located on the surface or embedded in the walls, based on the comparison of measurements of the amount of organic groups by elemental chemical analysis and by superficial volumetric determination with AgNO_3 ²⁸. They also used the same strategy to compare amino-functionalized MCM-41 and anionic-surfactant-templated mesoporous silica (AMS)²⁹. On the other hand, the adsorption of copper complexes over amino-functionalized Periodic Mesoporous Organosilicas (PMO's) was analysed in terms of accessibility of amino functional groups as well³⁰, but in this case a detailed study of metal coordination was needed for discussing about location and distribution of organic groups³¹. More recently, some research groups have studied the distribution of amino groups on mesostructured materials by analysing the UV spectrum of samples subjected to specific chemical reactions³²⁻³⁴. Functionalized MCM-41 materials and different aminopropylsilane molecules were studied by reacting amino groups with fluorescein

coupled with molecular UV spectroscopy³². Mono, di and tri-amino MCM-41 samples obtained by grafting in different solvents were treated to form cupric amino complexes, whose electronic spectrum allowed to elucidate the degree of site isolation of amino groups and the distribution of organoamines³³. Amino-modified SBA-15 silica materials obtained by grafting, co-condensation and polymerization were also used to determine the effective concentration of accessible amino groups by reaction with benzaldehyde derivatives and by UV spectroscopy³⁴.

In this paper, the distribution of amino groups incorporated to the mesostructured silica surface has been determined by a combination of transmission electron microscopy (TEM) and a staining technique of the functional groups. TEM provides direct and local information at the nanometric scale³⁵⁻³⁶ based on the image contrast, which is the result of the variation in electron density among the existing structures. However, organic molecules incorporated to mesostructured silicas have low atomic number elements, which exhibit little variation in electron density, so that alternative methods have to be used to achieve their efficient location. The staining technique has been proven useful in contrast enhancement of other type of materials, such as multiphase polymers³⁷. The staining agents are heavy atoms that are added to specific structures and can selectively interact with functional groups incorporated to the support. Thus, the functional groups are recognized because the presence of the staining agent changes the contrast with the whole structure, allowing to directly locate the position of functional groups by looking at the distribution of the staining agent.

This combination of techniques has been scarcely reported in the literature in order to identify the allocation of silanol, thiol and amino groups incorporated to mesostructured MCM-41 silica by using large transition metal clusters as staining agents³⁸⁻³⁹. Actually, this technique has been occasionally applied to demonstrate the selective

functionalization of inner and outer surfaces of the adsorbents by means of the reaction of vinyl organic moieties with palladium complexes⁴⁰ or by complexing the propylamino groups with iridium (III) chloride⁴¹, being the palladium and iridium metals the contrast agents in TEM micrographs.

Among the staining reagents used for detecting specific functional groups, both osmium and ruthenium tetroxide are considered as specific staining agents for amino groups³⁷.

Ruthenium tetroxide is known to be a stronger oxidizing agent than osmium tetroxide and it also exhibits fast diffusion. The expected reaction of amino groups with ruthenium tetroxide is the oxidation of the basic group and the formation of ruthenium dioxide, which can be easily detected by TEM.

In this work amino-functionalized SBA-15 materials that show interesting CO₂ adsorption properties have been studied by characterizing the amino group distribution on the silica surface, observing the effect of this distribution on the CO₂ adsorption performance. The incorporation of amino groups to SBA-15 was performed by grafting, co-condensation and impregnation procedures.

2. Experimental procedure

2.1. Synthesis of SBA-15 silica

SBA-15 mesoporous silica was synthesised according to Zhao et al.¹² using the triblock copolymer Pluronic P123 (triblock poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide), PEO₂₀PPO₇₀PEO₂₀) as structure directing agent and TEOS (tetraethoxysilane; (CH₃CH₂O)₄ Si) as silica source. Gel composition TEOS:Pluronic P123:HCl:H₂O was 1:0.017:5.8:163, carrying out the synthesis at 40 °C for 20 h. Further aging was performed by maintaining the suspension at 110 °C for 24 h.

Calcination at 550 °C using a heating rate of 1.8 °C/min was used to remove the surfactant from the formed porous structure.

2.2. Synthesis of amino-functionalized SBA-15 silica materials

The preparation of amino-functionalized materials was performed by three different procedures: grafting¹⁴, co-condensation⁴², and impregnation¹⁶.

Grafted materials with amino groups were obtained by refluxing 1 g of SBA-15 silica in 250 mL toluene with selected organosilanes for 24 h¹⁴. Three different aminosilanes were used: 3-(Trimethoxysilyl)propylamine [(H₂N-(CH₂)₃-Si(OCH₃)₃)], *N*-[3-(Trimethoxysilyl)propyl]ethylenediamine [(H₂N-(CH₂)₂-NH-(CH₂)₃-Si(OCH₃)₃)] and *N*'-(3-Trimethoxysilylpropyl)diethylenetriamine [(H₂N-(CH₂)₂-NH-(CH₂)₂-NH-(CH₂)₃-Si(OCH₃)₃)]. These molecules will be denoted as aminopropyl, AP (N); ethylenediaminopropyl, ED (NN); and diethylenetriaminopropyl, DT (NNN). The amount of aminosilane used in the synthesis was calculated by assuming a number of superficial silanol group concentration (1.7, 6 and 10 SiOH/ nm²) and a 1:1 stoichiometry reaction between silanol groups and organosilane moieties. Since the estimated silanol surface concentration value for silica calcined at 550 °C is approximately 1.7 SiOH/nm²⁴³, the three mentioned values of silanol surface concentration represent an excess above the stoichiometric value. Samples were named as G-SBA-15-*X*-(*n*), G referring to grafting, *X* to the organic moiety, *i.e.*, AP(N), ED(NN), or DT(NNN), and *n* to the number of silanol groups per unit surface in SBA-15, *i.e.*, 1.7, 6, or 10 SiOH/nm².

Co-condensed aminated SBA-15 silica materials were synthesised in a single step producing the condensation of TEOS and the organosilane in the reactive medium but maintaining a short TEOS prehydrolysis time (45 min) before the organosilane

addition⁴². The initial synthesis mixture was the following in all cases: 1 TEOS: 0.1 aminosilane: 0.018 P123: 6.4 HCl: 182 H₂O. This gel was stirred up at 40 °C for 20 h and the aging step was carried out at 110 °C for 24 h. Extraction with ethanol under reflux for 24 h was used to remove the template (140 mL ethanol per gram of solid). The resulting materials were named as C-SBA-15-N, C-SBA-15-NN, and C-SBA-15-NNN, now C referring to co-condensation.

Materials obtained by both procedures were filtered, washed with toluene and dried at room temperature, since previous studies showed that air-drying of functionalized samples at mild temperatures such as 110 °C leads to amino group decomposition¹⁴. Mesostructured silica SBA-15 was impregnated with an organic polymer, polyethyleneimine (PEI) with 800 units of molecular weight, which contains a high amount of amino groups in its structure¹⁶. The support was impregnated by adding different amounts of the organic polymer to obtain 10, 30, 50 and 70 % weight of organic component in the final product. The impregnation was carried out by dispersing 1 g of SBA-15 silica in a methanol solution of PEI polymer. The ratio SBA-15:methanol was maintained to 1:8 (wt.), while PEI:methanol relation subsequently varied. After stirring for 30 minutes, solvent was removed by drying at room temperature. The resulting solids were named as I-SBA-15-PEI-*x*, where *x* represents the weight percentage of PEI in the final solid and “I” refers to impregnation.

2.3. Chemical, textural, and structural characterization of synthesised materials

The nitrogen content, corresponding to the amino groups incorporated, was measured by elemental microanalysis on a CHNOS model Vario EL III of Elemental Analyses System GMHB.

Textural properties were determined from N₂ adsorption-desorption isotherms at -196 °C measured in a Micromeritics Tristar 3000 sorptometer. Surface area was calculated by using the B.E.T. equation (P/P_0 from 0.05 to 0.20) and the pore size distribution was obtained from the adsorption branch by means of the B.J.H. model assuming a cylindrical geometry of the pores⁴⁴. Degasification step prior to adsorption analyses was carried out under a nitrogen flux of 100 mL/min, at a temperature of 200 °C for pure silica SBA-15 and at 150 °C for organic-containing samples. Low-angle X-Ray diffraction measurements to check the mesoscopic order were performed on a powder Philips X-Pert MPD diffractometer using the K α Cu radiation.

2.4. Characterization by combining the staining technique and transmission electron microscopy.

The distribution of amino groups was determined by the selective fixation of RuO₄ over amino groups and its subsequent reduction to RuO₂. The high electronic density of this heavy metal makes the electron beam pass through it difficult when the sample is analysed by TEM. Thus, a specific darkening can be assigned to RuO₂ and, as a consequence, to the position of amino groups in the samples.

Following a general method for RuO₄ staining³⁷, SBA-15 samples have been exposed to the vapour of 0.5 % RuO₄ (*aq.*) for 15 min to stain amino groups. Previous studies⁴⁵⁻⁴⁷ have shown that a RuO₄ exposure time of 5, 8 or 10 min respectively are enough to stain the sample. Transmission electron micrographs were acquired on a Phillips Tecnai 20 electronic microscope working at 200 kV.

2.5. CO₂ adsorption analyses

Pure CO₂ adsorption-desorption isotherms were carried out in a Scientific Instruments HVPA-100 equipment, VTI, at 45 °C from 0 to 6 bar. Samples were previously outgassed at 110 °C under vacuum for 2 h. Sievert method was used to acquire isotherm points and two equilibrium criteria were jointly considered: a pressure drop below 0.2 mbar/3 min or a maximum equilibration time of 60 min.

3. Results and discussion

3.1. Physical-chemical characterization of samples

Table 1 shows the textural properties and nitrogen content obtained for pure SBA-15 and functionalized samples. As it was previously shown, grafted¹⁴, impregnated¹⁶ and co-condensed⁴² materials present a significant reduction in their textural properties (surface area and pore volume) compared to pure SBA-15 due to the presence of the organic agent. Comparatively, co-condensation method led to a lower reduction.

Also, low angle X-ray diffraction patterns (not shown here) confirmed the characteristic 2D hexagonal mesostructure of all samples, despite the reduced intensity of the diffraction peaks due to the organic content present in the pores.

Nitrogen content measured for co-condensed materials presents small values, in the range 1.3-2.7 %, showing a small extent of organic functionalization. Samples obtained by grafting and impregnation achieve much higher nitrogen content (3.6-8.0 % for grafting and 3.1-13.5 % for impregnation). It is noteworthy that although nitrogen content in the samples increases with the number of amino functional groups of the organosilane (AP (N) < ED (NN) < DT (NNN)), the molar amount of organic chain incorporated in the material slightly decreases in the order G-SBA-15-N-(6) > G-SBA-15-NN-(6) > G-SBA-15-NNN-(6), from 2.6 to 1.7 mmol g⁻¹. This fact has been previously observed in these systems⁴².

3.2. Distribution of organic functional groups by TEM

As a first step, the possible interaction of silanol groups of pure non-functionalized SBA-15 silica with the staining agent was checked. Fig. 1 shows the TEM micrographs for calcined SBA-15 before and after the staining treatment with RuO₄ (Figures 1a and 1b, 1c, respectively). As seen, images evidence the longitudinal arrangement of mesopores, characteristic of SBA-15 materials¹², showing clear areas corresponding to the empty pores and darker regions corresponding to pore walls. This contrast is the same in both cases, that is, clear and dark areas correspond to the same regions (pore cavities and pore walls respectively) regardless of the presence of RuO₄. This similarity between stained and non-stained SBA-15 verifies that RuO₄ does not interact with the silanol groups of the silica surface in the staining conditions used in this work.

3.2.1 Functionalization with amino groups by grafting.

Materials grafted with aminopropyl (AP (N)), ethylenediaminopropyl (ED (NN)), and diethylenetriaminopropyl (DT (NNN)) moieties supposing a silanol surface concentration of 6 SiOH/nm² have been firstly studied. Micrographs of samples stained with ruthenium are shown in Fig. 2. A different image contrast is now observed, depending on the number of amino groups per organic chain. TEM image of SBA-15 material functionalized with aminopropyl (containing only one amino group) G-SBA-15-N-(6) (Fig. 2a), shows clear areas that correspond to the empty pores, and darker regions that correspond to the pore walls, similarly to pure SBA-15 siliceous material. Also, a scattering of black dots, corresponding to RuO₄ particles interacting with the amino groups of the functionalized material, is observed. Regarding their size, black spots cannot be assigned to individual ruthenium atoms interacting with amino

groups, so they may represent either small groups of nearby amino moieties individually reacting with RuO₄ or else several ruthenium atoms around a single amino group. As shown, the amino groups appear as discrete regions homogeneously distributed along the sample pores.

As the number of amino groups per organosilane molecule increases, the organic content of the material increases too (G-SBA-15-N-(6) < G-SBA-15-NN-(6) < G-SBA-15-NNN-(6)), as observed in Table 1. Consequently, the amino groups present in the pores are closer to each other, as revealed when staining with RuO₄, resulting in TEM images that show a more intense and continuous contrast along the pores (Fig. 2b). Now, in the sample G-SBA-15-NN-(6), darker lines correspond to RuO₂ filled pores, while lighter areas correspond to the pore walls.

TEM micrograph of the highest loaded sample in this series, G-SBA-15-NNN-(6) (Fig. 2c) shows that the amino functional groups are practically filling up the pores as well as covering the outer surface of the particles, as shown by the dark-light contrast observed. Besides, G-SBA-15-NNN-(6) material has also been analysed without performing the staining step to check if amino groups are visible directly by TEM. Fig. 2d shows the corresponding micrograph, where it can be seen that the unstained sample presents a distribution of pore cavities (light) and pore walls (dark) similar to the silica SBA-15 before functionalization. Thus, it clearly shows that amino groups are not detectable by TEM if the staining step is not performed.

Following with the analysis of SBA-15 grafted with DT (NNN), TEM image of RuO₄ stained G-SBA-15-NNN-(1.7) is shown in Fig. 3. Here, Fig. 3a exhibits a transversal array of channels where the mentioned contrast is clearly shown. Again, pore channels appear as black circles in a hexagonal array due to the proximity of several amino groups which, after the interaction with RuO₄ appear as continuous black areas. On the

contrary, surrounding silica walls are lighter. Pore channels appear now much darker, since they are filled up with amino groups and those have been stained with RuO_4 , while silica walls do not contain organic groups. Fig. 3b shows the same contrast, now corresponding to a longitudinal view of the pore structure (same sample). Finally, TEM image of G-SBA-15-NNN-(10) material, the sample with the highest nitrogen content, can be observed in Fig. 3c, where little contrast is found, being the channels-walls distribution hardly visible. This effect cannot be only assigned to a highly functionalization of the inner pores. Also, the outer surface may be similarly functionalized with DT (NNN), thus virtually avoiding the pore structure of the particle to be distinguished.

3.2.2. Functionalization with amino groups by co-condensation.

Amino-functionalized SBA-15 materials obtained by the one-step co-condensation synthesis procedure, named C-SBA-15-N, C-SBA-15-NN, and C-SBA-15-NNN, have also been compared with the grafted samples. A micrograph for non-stained C-SBA-15-N sample is shown in Fig. 4a, where the typical longitudinal channels are observed. TEM micrographs of C-SBA-15-N, C-SBA-15-NN, and C-SBA-15-NNN samples after RuO_4 staining are also shown in Fig. 4b, 4c and 4d respectively. The three images exhibit a considerable number of black dots, assigned to ruthenium species fixed over amino groups homogeneously distributed in the sample, including pores and walls, as observed when comparing figures 4b and 3b. This appearance can be explained by taking into account the synthesis method used in this case. During the hydrolysis step, the highly acidic synthesis medium leads to the protonation of amino groups of the aminosilanes. Protonated species can cross-link with the alcoxysilane precursor during the condensation step and as a consequence the organosilanes used are eventually deposited both in the pore channels and inside the walls of the resulting materials⁴⁸.

Therefore, TEM images of samples obtained by co-condensation show the presence of amino groups in the silica walls as well as inside the pores. This was not the case of grafted samples, where high contrast dots were only found within the channels, as amino groups are only incorporated to the silica surface.

When the number of amino groups in the organosilane increases, the amount of black ruthenium dots existing in the sample also increases. This effect leads to a hardly distinguishable structure in the sample C-SBA-15-NNN, which contains the highest number of amino groups.

3.2.3. Functionalization with amino groups by impregnation.

SBA-15 samples impregnated with the branched type of polyethyleneimine polymer, I-SBA-15-PEI-10, I-SBA-15-PEI-30, and I-SBA-15-PEI-50, which contain 10, 30 and 50 % (wt.) of PEI respectively, have been compared with the rest of the functionalized materials.

TEM characterization of stained samples has led to critical findings about the preparation procedure. Fig. 5 shows a micrograph corresponding to the I-SBA-15-PEI-10, which contains 3.1 % of nitrogen (Fig. 5a), along with two images of I-SBA-15-PEI-50, with 13.5 % N (Figures 5b and 5c). Both samples were stained with RuO_4 . As seen, low nitrogen sample evidences a heterogeneous PEI loading, where low and high coated areas can be distinguished (Fig. 5a). This sample has also shown the existence of non-covered particles (images not shown), suggesting a heterogeneous loading of PEI polymer.

TEM images of I-SBA-15-PEI-50, corresponding to the highest amount of nitrogen, show a high contrast (Figures 5b and 5c). However, its appearance is remarkably different in comparison with highly loaded materials obtained by grafting (Fig. 3c). As

it can be seen, RuO₂ particles are located on the external surface of the impregnated sample, but the pores do not seem to be significantly occupied by the staining agent. Considering the pore volume of SBA-15 pure silica, the maximum PEI amount that could be incorporated to the pores of this material is 53.6 %¹⁶. However, although this sample contains 50 % of PEI, it is mainly located on the external surface. Moreover, there are also many regions in this sample which have no amino groups (not shown here), similarly to I-SBA-15-PEI-10 sample. Therefore, we conclude that pore diffusion of PEI polymer is much more difficult than organosilane pore diffusion in grafting processes, and consequently that the impregnation technique leads to heterogeneous solids, where PEI does not completely fill up the pores, but stays on the particle external surface. This interpretation has not been found in the literature till now, as the complete pore filling with PEI has been usually claimed.

3.3. CO₂ adsorption over functionalized samples.

After studying the distribution of amino groups in the mesoporous SBA-15 silica samples functionalized by chemical and physical procedures, their CO₂ adsorption properties were evaluated. Pure CO₂ isotherms of the materials carried out at 45 °C are shown in Fig. 6. The corresponding adsorption capacities (mg CO₂/g sample) along with the nitrogen content and CO₂ capture efficiency values (mol CO₂/mol N) are shown for each sample in Table 2. Adsorption capacity values at a partial pressure of 0.15 bar are included in Table 2, as this partial pressure corresponds to the existing CO₂ concentration in the exhaust gases of a typical coal-fired thermal power station. CO₂ adsorption isotherms present marked differences in their behaviour depending on the presence of amino groups. Thus, siliceous SBA-15 material shows small adsorption values at low partial pressures and significantly higher values at higher pressures, as a

pressure-dependent isotherm pattern is revealed. Also, the process is completely reversible, as the desorption branch of the isotherm is coincident with the adsorption branch. These characteristics are indicative of physical adsorption processes, as observed for activated carbons⁴⁹ and zeolites⁵⁰.

In contrast, SBA-15 functionalized materials (mainly grafted and impregnated samples) show a different behaviour: CO₂ adsorption capacity at low pressures is much higher now, and pressure dependence is reduced, since uptake values at higher pressures do not increase as much as for SBA-15 sample. Besides, the CO₂ adsorption process is not completely reversible in the adsorption conditions, as the desorption and adsorption branches do not coincide. These features, characteristic of chemical adsorption, are more pronounced for higher loaded samples. However, less loaded samples and co-condensated materials are closer to the physisorption behaviour, as they contain few amino groups or these organic moieties are not significantly contributing to the chemical adsorption mechanism.

Grafted samples show an adsorption capacity at 0.15 bar ranging from 33.0 to 60.8 mg CO₂/g depending on the nitrogen content of the sample. Thus, G-SBA-15-NNN-(1.7), with a nitrogen content of 5.3 %, reaches an adsorption capacity of 45.3 mg CO₂/g at 0.15 bar, while G-SBA-15-NNN-(6) contains 7.3 % nitrogen and adsorbs up to 60.8 mg CO₂/g .

The efficiency of amino groups for CO₂ adsorption of grafted samples is in the range 0.23-0.38 mol CO₂/mol N depending on the organosilane chain, AP (N), ED (NN) or DT (NNN), and the amount of organosilane used for grafting. While the maximum efficiency obtained for DT (NNN) molecule is 0.32-0.33 mol CO₂/mol N (for G-SBA-15-NNN-(6) and G-SBA-15-NNN-(10) respectively), the G-SBA-15-N-(6) sample presents a value of 0.38 mol CO₂/mol N. Thus, aminopropyl molecule, which

has only one amino group, is shown to be more effective for CO₂ adsorption in terms of efficient use of amino groups, or in other words, the reaction of CO₂ molecules with every amino group present in the sample seems to be favoured by the presence of just one amino group in the organic chain.

When a higher content of DT (NNN) is grafted over the surface, not only the total nitrogen content increases (6.3, 7.3, and 8.0 % for 1.6, 6, and 10 SiOH/nm² respectively, Table 2), but also the concentration of organic chains in the surface (1.5, 1.7 and 1.9 mmol/g respectively, Table 1) does. The higher packing of aminated organosilanes favours the CO₂ interaction with amino groups from nearby chains, consequently increasing the efficiency of the process (0.23, 0.33 and 0.32 mol CO₂/mol N respectively, Table 2). When discussing efficiency data, it must be noted that 0.50 mol CO₂/mol N is the maximum achievable value in dry conditions, since one mole of CO₂ reacts with two adjacent amino groups, according to the reaction mechanism for the CO₂ chemisorption⁴⁸.

Samples obtained by co-condensation show a very low CO₂ adsorption capacity in all cases. Some values are even lower than the corresponding to the SBA-15 siliceous support, as they range from 1.9 to 3.7 mg CO₂/g at 0.15 bar. The efficiency of amino groups in these samples is also very low, ranging from 0.11 to 0.22 mol CO₂/mol N. PEI-impregnated materials reach the highest CO₂ adsorption capacities, in the range 14.1-71.2 mg CO₂/g s at 0.15 bar, and also show the highest nitrogen content (3.1-13.5 %). However, CO₂ adsorption efficiency shows a significant drop as the organic loading is increased. While I-SBA-15-PEI-10 has an efficiency of 0.25 mol CO₂/mol N, this parameter drops down to 0.18 for I-SBA-15-PEI-50, which has a higher PEI content.

These results can be explained by taking into account the distribution of amino groups previously observed by TEM. First of all, the very low CO₂ adsorption observed for co-condensed samples cannot be explained only by the small amount of nitrogen incorporated (1.3-2.7 %), but also by the fact that the one-step synthesis method produces the scattering of the aminated organosilanes within the materials, both through the pores and imbedded in the walls. It is also very likely that amino groups are still protonated in these samples⁴⁸ and thus, they are not able to react with CO₂ molecules, giving as a result a very low efficiency in CO₂ adsorption.

TEM images obtained for PEI-impregnated samples show that the polymer is heterogeneously incorporated, covering mainly the external surface of siliceous particles. Hence, a thicker layer of polymer is deposited around SBA-15 particles when a higher amount of PEI is used, increasing the difficulty of CO₂ diffusion within the material. As a consequence, the amino groups inside the pores or located deep in the PEI layer scarcely react with CO₂, reducing the CO₂ adsorption efficiency.

Grafted samples present a higher efficiency than co-condensated and impregnated samples. This is mainly due to the distribution of organosilane molecules in the silica material, mostly located in the porous surface of the particles. In this case CO₂ diffusion through the channels is facilitated, and thus, carbon dioxide easily reaches practically all amino groups. Additionally, organosilanes grafted on the external surface of the particles or in the pore entrance do not present a significant diffusion hindrance, as their molecule length is much shorter than the pore diameter of SBA-15 material.

4. Conclusions

Co-condensation, grafting and impregnation techniques are compared as procedures to obtain amino SBA-15 adsorbents for CO₂ capture. However, the resulting materials

show large differences in the nitrogen content incorporated and in the CO₂ adsorption uptake and efficiency values.

Here, the dissimilar behaviour of amino groups in CO₂ capture is related to the specific position of amino groups throughout the siliceous structure of SBA-15, which has been determined by the combination of Transmission Electron Microscopy (TEM) with a staining technique using RuO₄. Samples obtained by co-condensation, with low nitrogen contents, exhibit their organic groups located both in the surface and inside the silica walls, not being available for CO₂ capture. Impregnation of SBA-15 with PEI leads to the highest degree of functionalization, but amino groups are located mainly in the external surface of SBA-15, forming a thick layer that drastically limits CO₂ diffusion and pore access. Grafting materials achieve a considerable amount of organic loading, amino groups being mainly located inside pore channels, and thus favouring CO₂ diffusion through the whole structure.

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References

- [1] J.T. Houghton, G.J. Jenkins (Eds.) *IPCC First Assessment Report 1990*, Cambridge Univ. Press, New York, 1990.
- [2] B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer (Eds.) *IPCC Special Report on Carbon Dioxide Capture and Storage*, Cambridge Univ. Press, Cambridge & New York, 2005.

- [3] *Kyoto Protocol to the United Nations Framework Convention on Climate Change*, United Nations, 1998.
- [4] *Carbon sequestration. State of Science*. Office of Science and Office of Fossil Energy. US Department of Energy. DOE/OS-FE, Washington D. C., 1999
- [5] P. Tontiwachwuthikul, A. Meisen, C. J. J. Lim, *Chem. Eng. Data.* 36 (1991) 130-133.
- [6] S. Choi, J. H. Drese, C. W. Jones, *ChemSusChem* 2 (2009) 796-854.
- [7] C. T. Kresge, M.E. Leonowicz, W. T. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* 359 (1992) 710-712.
- [8] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* 63 (1990), 988-992.
- [9] A. Taguchi, F. Schüth., *Micropor. Mesopor. Mater.* 77 (2005) 1-45.
- [10] P. T. Tanev, T. J. Pinnavaia, *Science*, 267 (1995) 865-867.
- [11] S. A. Bagshaw, E. Prouzet, T. J. Pinnavaia, *Science* 269 (1995) 1242-1244.
- [12] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* 279 (1998) 548-552.
- [13] G. P. Knowles, J. V. Delaney, A. L. Chaffe, *Ind. Eng. Chem. Res.* 45 (2006) 2626-2633.
- [14] G. Calleja, R. Sanz, A. Arencibia, E. S. Sanz-Pérez, *Top. Catal.* 54 (2011) 135-145.
- [15] X. C. Xu, C. S. Song, J. M. Andersen, B. G. Miller, A. W. T. Scaroni, *Energy Fuels* 16 (2002) 1463-1469.
- [16] R. Sanz, G. Calleja, A. Arencibia, E. S. Sanz-Pérez, *Appl. Surf. Sci.* 256 (2010) 5323-5328.
- [17] J. M. Rosenholm, A. Penninkangas, M. Linden, *Chem. Comm.* (2006), 3909-3911.

- [18] M. B. Yue, L. B. Sun, Y. Cao, Y. Wang, Z. J. Wang, J. H. Zhu, *Chem. Eur. J.* 14 (2008) 3442-3451.
- [19] M. B. Yue, Y. Chun, Y. Cao, X. Dong, J. H. Zhu, *Adv. Funct. Mater.* 16 (2006) 1717-1722.
- [20] A. Stein, B. J. Melde, R. C. Schrodin, *Adv. Mater.* 12 (2000) 1403-1419.
- [21] A. Vinu, K. Z. Hossain, K. Ariga, *J. Nanosci. Nanotechnol.* 5 (2005) 347-371.
- [22] M. Lim, A. Stein, *Chem. Mater.* 11 (1999) 3285-3295.
- [23] U. G. Singh, R.T. Williams, K.R. Hallan, G.C. Allen, *J. Solid State Chem.* 178 (2005) 3405-3413.
- [24] L. Mercier, T. J. Pinnavaia, *Environ. Sci. Technol.* 32 (1998) 2749-2754.
- [25] J. Aguado, J. M. Arsuaga, A. Arencibia, *Ind. Eng. Chem. Res.* 44 (2005) 3665-3671.
- [26] J. Aguado, J. M. Arsuaga, A. Arencibia, *Micropor. Mesopor. Mater.* 109 (2008) 513-524.
- [27] A. Walcarius, C. Delacôte. *Chem. Mater.* 15 (2003) 4181-4192.
- [28] T. Yokoi, H. Yoshitake, T. Tatsumi, *J. Mater. Chem.* 14 (2004) 951-957.
- [29] T. Yokoi, H. T. Yoshitake, Y. Yamada, Kubota, T. Tatsumi, *J. Mater. Chem.* 16 (2006) 1125-1135.
- [30] M. C. Burleigh, M. A. Marlowitz, M.S. Spector, B.P. Gaber, *Chem. Mater.* 13 (2001) 4760-4766.
- [31] S. D. Kelly, K. M. Kemmer, G. E. Fryxell, J. Liu, S. V. Mattigod, K. F. Ferris, *J. Phys. Chem. B* 105 (2001) 6337-6346.
- [32] H. Salmio, D. Brühwiler, *J. Phys. Chem. C* 111 (2007) 923-929.
- [33] K.K. Sharma, R. P. Buckley, T. Asefa, *Langmuir* 24 (2008) 14306-14320.
- [34] J. M. Roshenholm, M. Linden, *Chem. Mater.* 19 (2007) 5023-5034.

- [35] I. Díaz, V. Alfredsson, Y. Sakamoto. *Current Opinion in Colloid & Interface Science* 11 (2006) 302-307.
- [36] W. T. Zhou, J. M. Thomas, *Current Opinion in Colloid & Interface Science* 5 (2001) 75-83.
- [37] L. C. Sawyer, D. T. Grubb (Eds.) *Polymer microscopy*, Chapman & Hall, London, 1996.
- [38] D. S. Shephard, W. T. Zhou, T. Maschmeyer, J. M. Matters, C. L. Roper, S. Parsons, B. F. G. Johnson, M. J. Duer, *Angew. Chem. Int. Ed.* 37 (1998) 2719-2723.
- [39] S. Hermans, S. Sadasivan, C. M. G. Judkins, B. F. G. Johnson, S. Mann, D. Khushalani, *Adv. Mater.* 15 (2003) 1853-1857.
- [40] C. M. Yang, H. A. Lin, B. Zibrowius, B. Spliethoff, F. Schüth, S. C. Liou, M. W. Chu, C. H. Chen, *Chem. Mater.* 19 (2007) 3205-3211.
- [41] J. Kecht, A. Schlossbauer, T. Bein, *Chem. Mater.* 20 (2008) 7207-7214.
- [42] J. Aguado, J. M. Arsuaga, A. Arencibia, M. Lindo, V. Gascón, *J. Hazard. Mater.* 163 (2009) 213-221.
- [43] P. Van der Voort, I. Gills-D'Hamers, K. C. Vrancken, E. F. Vansant, *Faraday Trans.* 87 (1991) 3899-3905.
- [44] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscon, R. A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603-619.
- [45] F. Stricker, Y. Thomann, R. Mülhaupt. *J. Appl. Polymer Sci.* 68 (1998) 1891-1901.
- [46] J. K. Kim, D. S. Jung. *Polymer* 34 (1993) 4613-4624.
- [47] S. Setz, F. Stricker, J. Kerssler, T. Duschek, R. Mülhaupt. *J. Appl. Polymer Sci.* 59 (1996) 1117-1128.
- [48] A. S. Maria Chong, X. S. Zhao, A. T. Kustedjo, S. Z. Qiao, *Micropor. Mesopor. Mater.* 72 (2004) 33-42.

[49] T. C. Drage, J. M. Blackman, C. Pevida, C. E. Snape, *Energy & Fuels* 23 (2009) 2790-2796.

[50] S. Cavenati, C. A. Grande, A. E. Rodrigues, *J. Chem. Eng. Data* 19 (2004) 1095-1101.

[51] M. Caplow, *J. Am. Chem. Soc.* 24 (1968) 6795-6803.

Figure captions.

Fig. 1. TEM micrographs of pure silica SBA-15: a) before staining with RuO₄; b) and c) after staining.

Fig. 2. TEM micrographs of samples stained with RuO₄: (a) G-SBA-15-N-(6), (b) G-SBA-15-NN-(6), (c) G-SBA-15-NNN-(6) and (d) TEM micrograph of G-SBA-15-NNN-(6) not stained with RuO₄.

Fig. 3. TEM micrographs of samples stained with RuO₄: (a) G-SBA-15-NNN-(1.7), transversal view; (b) G-SBA-15-NNN-(1.7), longitudinal view and (c) G-SBA-15-NNN-(10).

Fig. 4. TEM micrographs of C-SBA-15-N: (a) without staining treatment, (b) longitudinal view after staining treatment with RuO₄. TEM micrographs Ru-stained (c) C-SBA-15-NN and (d) C-SBA-15-NNN.

Fig. 5. TEM micrographs of Ru-stained samples: (a) I-SBA-15-PEI-10 and (b) I-SBA-15-PEI-50, longitudinal view; (c) I-SBA-15-PEI-50, transversal view.

Fig. 6. Pure CO₂ adsorption-desorption isotherms at 45 °C on pure siliceous SBA-15 support and functionalized SBA-15 materials obtained by: (a) grafting, (b) co-condensation and (c) impregnation.