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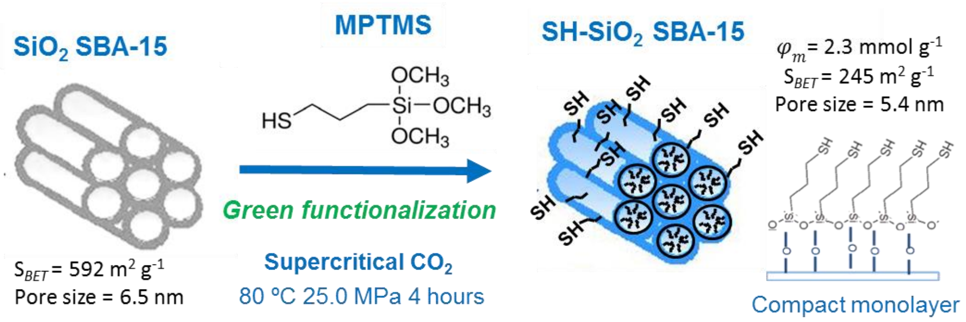

Highlights

- Thiol functionalization of SBA-15 was performed in $scCO_2$ at 40-150ºC and 15-29 MPa.
- Grafting density increased with temperature, CO_2 density, time and stirring.
- S_{BET} and pore size decreased as grafting density increased.
- A compact monolayer was formed at temperatures of 80 ºC or higher.
- The sample prepared in $scCO_2$ at 80 ºC, 25.0 MPa had high grafting density and S_{BET}.

THIOL GROUP FUNCTIONALIZATION OF MESOPOROUS SiO_2 SBA-15 USING SUPERCRITICAL CO_2

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ABSTRACT

Chemical modification of mesoporous SiO_2 SBA-15 with thiol groups was performed using mercaptopropyltrimethoxysilane (MPTMS) dissolved in supercritical CO_2 ($scCO_2$). Thiol groups serve as adsorbents for the selective removal of contaminant metal cations and in catalysis. Functionalization was carried out in $scCO_2$ at temperatures ranging from 40 to 150 ºC and pressures from 15.0 to 29.0 MPa. For comparison purposes, the reaction was also performed in toluene at 80 and 110 ºC. As opposed to toluene, $scCO_2$ is considered a green solvent. Grafting of the thiol groups was confirmed by FTIR spectroscopy, thermogravimetric analysis (TGA) and elemental analysis. Grafting density and surface coverage of the materials modified using $scCO_2$ increased with temperature, CO_2 density, time and stirring and varied from 1.3 to 4.4 mmol g^{-1} and from 1.3 to 4.0 molecules nm^{-2}, respectively. On the other hand, surface area and pore size decreased as grafting density increased. At temperatures of 80 ºC or higher, the pore size remained constant, suggesting the formation of a compact monolayer. Modification at higher temperatures led to larger grafting densities but very low surface areas. Assuming total hydrolysis and condensation of the precursor, the optimum grafting density and surface coverage of 2.3 mmol g^{-1} and 2.4 molecules nm^{-2}, respectively, were obtained in $scCO_2$ at 80 ºC and 25.0 MPa for 4 h. Grafting densities of the samples prepared in toluene were by far much lower than those obtained using $scCO_2$ at lower temperatures and shorter times, which demonstrates the advantages of CO_2 as a green functionalization medium.

Keywords: Surface modification, Supercritical fluids, Sustainable Chemistry, Mesoporous, SiO_2 SBA-15.

1. INTRODUCTION

Chemical modification of metal oxide surfaces is performed to improve the physical and chemical properties of the materials such as roughness, hydrophilicity, surface energy, biocompatibility, reactivity… It is currently used to prepare stationary phases in chromatography,[1] biocompatible surfaces,[2] environmental sorbents,[3, 4] heterogeneous catalysts[5] and sensors[6] among others. Stabilization of metal nanoparticles is also performed by functionalization with organic ligands.[7] Furthermore, by proper control of the surface properties, adhesion at interfaces can be improved.[8]

In particular, the surface modification of mesoporous silica materials with thiol groups has been applied to the preparation of materials for the selective removal of cations such as Hg^{2+}, Cd^{2+} , Pb^{2+}, Cu^{2+} and Cr^{3+}.[9, 10] Thiol groups may also act as binding sites for catalytic complexes, allowing the incorporation of many catalytic species.[11] Through oxidation of the thiol groups to sulfonic acid groups these materials may become catalysts themselves.[12, 13]

Thiols groups can be introduced by co-condensation during the synthesis[14] or by post-synthetic grafting.[15] Co-condensation of ordered mesoporous silica materials is challenging because it generally yields less ordered structures, and some of the functional groups become buried into the structure. On the other hand, the surface modification by post-synthesis covalent attachment is constrained by the number of reactive surface silanol groups, although, in principle, all the functional groups generated are accessible. Furthermore, the original support structure is preserved, although the pore size decreases.

Surface modification of SiO_2 and other metal oxide surfaces by post-synthetic grafting has been previously carried out using supercritical CO_2 ($scCO_2$). [16, 17] $scCO_2$ is considered a green solvent because it is nontoxic, non-flammable, has a moderate critical temperature and pressure (T_c = 31.1 ºC, P_c = 7.38 MPa) [18]. Furthermore CO_2 is a gas at atmospheric pressure and does not leave any residue. Most of the CO_2 used nowadays is obtained as a sub-product of many industrial processes.

The large solubility of many silane precursors (alkoxy and chloro silanes) in $scCO_2$ at moderate pressure and temperature conditions and the low viscosity, surface tension and enhanced diffusivity of the supercritical solutions, allow the efficient penetration of highly porous materials. The reaction generally involves the hydrolysis of the precursor and its condensation with the -OH groups from the SiO_2 surface or other hydrolyzed molecule precursors. Tripp and Combes studied the interaction of $scCO_2$ with fumed silica using infrared spectroscopy.[19] They pointed out the drying character of $scCO_2$ that can remove adsorbed water from the surface increasing the amount of accessible silanol groups on the surface. Thus the surface reaction of the precursor with the metal oxide surface is favored at these conditions.

Our group has recently reported the sustainable functionalization of mesoporous SiO_2 SBA-15 with amine groups in $scCO_2$. [20, 21] In comparison to the conventional functionalization process using toxic organic solvents, modification using $scCO_2$ was performed at lower temperature and shorter times and led to larger grafting densities. The materials were used as selective CO_2 sorbents in carbon capture technology. Similarly, Lopez-Aranguren et al. [22] have applied the supercritical functionalization process to the modification of the internal surface of silica porous substrates of diverse pore architecture showing that functionalization in $scCO_2$ preserved the porous character of the materials.

In this communication we report the surface modification of mesoporous silica SBA-15 with thiol groups in $scCO_2$. There are a few reports on the incorporation of thiol groups by reaction of mercaptopropyltrimethoxysilane (MPTMS) in $scCO_2$ on different SiO_2 supports. Shin et al. [23] reported the surface modification of microporous zeolites at 150 ºC and 52 MPa. The same pressure and temperature conditions were chosen by Zemanian et al. [24] to modify mesoporous SiO_2 MCM-41. Rebiscoul et al. [25] modified the surface of oxidized Si wafers at much more moderate pressure and temperature conditions (40 ºC and 10.9 MPa). A small amount of cosolvent (acetone or *N*-methyl-2-pyrrolidone, NMP) was used to improve precursor solubility. Finally Ashu-Arrah et al. [26] recently modified different porous SiO_2 commercial supports at 40-100 ºC and 41.4 MPa. The wide range of experimental conditions used in the different publications from 40 to 150 ºC and 10.9 and 52 MPa and the high pressures used in most of the reports, points out the need to perform a more systematic study of the role of the different variables on the process.

We have previously studied the phase diagram of MPTMS and CO_2.[27] Full miscibility of both components was achieved at 40, 50 and 60 ºC above 8.7, 10.2 and 12.3 MPa, respectively. Therefore, the high pressures employed in some of the surface modification experiments are not justified based on solubility requirements.

2. MATERIALS AND METHODS

2.1 MATERIALS

Tetraethylorthosilicate (TEOS, 99+% pure), poly(ethyleneglycol)–block–poly(propylene glycol)–block–poly(ethylenegly-col) (Mw = 5800) (PEO–PPO–PEO), (mercaptopropyltrimethoxysilane (MPTMS, purity>95%) and toluene (>99.5% pure) were obtained from Sigma–Aldrich and used as received. CO_2 (purity > 99.99%) was supplied by Air Liquide. Mesoporous silica SBA-15 was prepared following a procedure similar to that described by Zhao et al.[28, 29] Two different samples with BET surface areas of 592 and 674 m^2 g^{-1} were obtained.

2.2. SURFACE MODIFICATION OF SILICA SBA-15 IN SUPERCRITICAL CO_2

Most experiments were conducted in a ca. 65 cm^3 custom-made stainless steel high-pressure reactor in the batch mode. A few experiments were performed in a 100 cm^3 stirred high-pressure Bolted Closure reactor (Autoclave Eng.).

In the smaller reactor, the liquid MPTMS was place in a glass vial and the mesoporous silica SBA-15 was wrapped in a filter paper. In a typical experiment, ca. 100 mg of SiO_2 SBA-15 was treated with 0.5 or 1 g of MPTMS. A large molar excess was stablished considering a maximum silanol content of 3.7 OH nm^{-2} [30]. Experiments were performed at 40, 60, 80 and 100 ºC and 15.0 and 25.0 MPa. At 40-80 ºC, the small reactor containing the support and reagent was immersed in a thermostatic bath (PolyScience) and filled with CO_2 by means of a high-pressure syringe pump (Isco, Inc. Model 260D) at the desired temperature and pressure. At 100 ºC, a heating aluminum jacket connected to a PDI temperature controller (Micromega, model CN77322) was used instead. No stirring was used in these experiments. Temperature was measured using a type J calibrated thermocouple. The pressure was measured using a pressure transducer (Gems). A safety valve (Swagelok) was fitted to the reactor. The reaction proceeded for 1-8 hour depending on the experiments.

A few samples were prepared using the larger stirred high-pressure reactor at 80, 100 and 150 ºC. The reactor is equipped with a heating jacket connected to PDI controller to reach the desired temperature. The support was loaded into a basket fitted to the upper part of the reactor, whilst MPTMS was placed directly at the bottom of the reactor. The reactor was then filled with CO_2 using the high-pressure syringe pump at the same temperature up to the given pressure. The reactor was provided with an impeller stirrer which was agitated at 200 rpm. The temperature was measured using a K-type thermocouple. The pressure was measured using a pressure gauge. A rupture disk was fitted to the reactor. Reaction time for these experiments was fixed to 4 hours.

After the stablished reaction time, the reactor was extracted with $scCO_2$ at the reaction pressure and temperature at a flow rate of 1–2 mL min^{-1} during 60 min and was slowly depressurized through a needle valve in about 30 min. Samples were dried at 110 ºC under vacuum for 4 h.

2.4. SURFACE MODIFICATION OF SILICA SBA-15 IN TOLUENE

For comparison purposes, the SiO_2 SBA-15 was functionalized in toluene at 80 ºC and 110 ºC. Approximately 200 mg of silica SBA-15 and 1 or 2 g of MPTMS were loaded into a two-neck round-bottom glass flask containing 50 cm^3 of toluene fitted to a condenser. The glass flask was then immersed in a silicon oil bath set at the working temperature using a temperature-controlled stirring hot plate with an external temperature probe and was purged with N_2. The reaction was allowed to proceed for 24 h with gentle stirring. After reaction, the thiol-modified SiO_2-SBA-15 was filtered and washed with copious amounts of toluene and then ethanol. The recovered solid was dried at 100 ºC in a natural convection oven for 24 h.

2.4. MATERIALS CHARACTERIZATION

Materials were characterized using Fourier Transform Infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), elemental analysis and N_2-adsorption. FTIR spectra of the powdered materials were recorded as KBr pellets on an IR Perkin Elmer Spectrometer. At a spectral resolution of 4.0 cm^{-1}, 25 interferograms have been co-added. TGA of the samples was obtained on a SDT – Q600 at a heating rate of 10 ºC/min in N_2 flow (100 ml/min). Elemental analysis was performed on a LECO CHNS-932 microanalyser. The uncertainties in the elemental analysis were %C ± 0.26, %H ± 0.24 %N ± 0.25 and %S ±0.35. Low angle XRD patterns of the mesoporous materials were collected on a XPERT-Alpha1 diffractometer with Cu K-α radiation on the transmission mode and were recorded at 2θ values between 0.1 and 3º.

N_2 adsorption/desorption isotherms at 77 K were obtained using a Micromeritics ASAP-2020. Prior to adsorption measurements, samples were out-gassed at 110 ºC and ~10^{-1} Pa for 4 h. Isotherms were analyzed using standard procedures.[31] The BET equation was used for specific surface calculations. The total pore volume was estimated from the amount adsorbed at a relative pressure of 0.995. The pore size distributions were calculated using the Barrett, Joyner and Halenda (BJH) method for a cylindrical pore model corrected by the statistical thickness using the adsorption and desorption branches of the isotherms. The micropore volume was determined using the t-plot method. The actual pore size was estimated from the adsorption branch of the isotherm as was reported by Zhao et al. [29]

3. RESULTS AND DISCUSSION

Silica SBA-15 was chosen as the support to be modified because of its high surface area and pore volume. The support is formed by a hexagonal array of cylindrical mesopores which are interconnected by smaller micro and mesopores. The low-angle XRD pattern of the substrate is given in the Supplementary data. Three well resolved peaks were indexed according to the two dimensional *P6m* hexagonal symmetry.

Functionalization of mesoporous SiO_2 SBA-15 with MPTMS was carried out in $scCO_2$ at 40, 60, 80 and 100 ºC and 150 ºC and 15.0, 25.0 and 29.0 MPa. Reaction time was varied from 1 to 8 h and 5:1 and 10:1 precursor to support mass ratios (large precursor excess) were used. At 60 ºC, MPTMS and CO_2 are fully miscible above 12.3 MPa. [27] For comparison purposes, samples were also modified following the conventional method in toluene at 80 and 110 ºC. The experiments performed are summarized in Table 1.

Figure 1 depicts the possible reaction mechanism involving the hydrolysis of the precursor (i) and its condensation with the -OH groups from the SiO_2 surface or other neighboring molecule precursors (ii). Although in most experiments, water was not deliberately introduced into the system, the presence of adsorbed water on the silica surface, which is extracted in $scCO_2$, seems to be enough to initiate the reaction. Considering the surface reaction with the silanol groups of the surface a large number of possible structures can be envisioned, including partially hydrolyzed and condensed structures (A, B and D), those fully condensed and isolated (D) and those fully condensed forming a monolayer (E), among others. The polymerization reaction in the fluid phase is also possible, leading eventually to an oligomer that can be adsorbed at the sample surface forming a thick polymer condensed layer (not shown here).

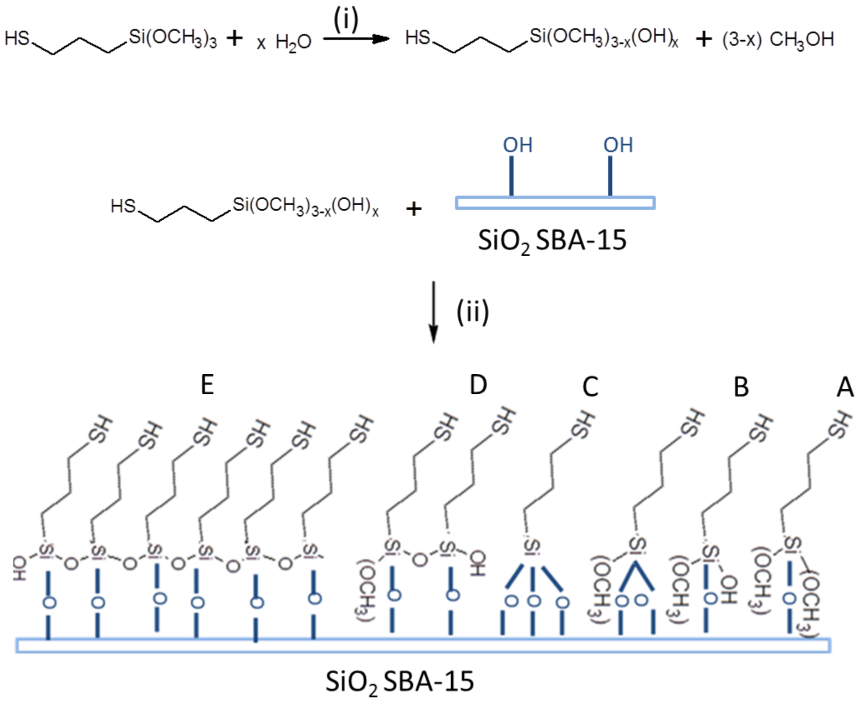

Figure 1- Possible mechanism for the surface reaction between MPTMS and SiO_2 SBA-15.

Figure 2 shows the FTIR spectra of sample 6 functionalized in $scCO_2$ at 80 ºC and 25.0 MPa for 4 hours and sample 13 modified in toluene at 110 ºC for 24 hours. FTIR spectra show the characteristic C-H stretching vibrations at 2962, 2937, 2892 and 2852 cm^{-1} indicative of both ($–CH_2–$) and ($–CH_3$) groups, which clearly indicate the presence of the organic groups attached to the silica surface, including unreacted precursor or partially hydrolyzed forms on the support surface. The absorption band at 1460 cm^{-1} characteristic of the bending mode of (–CH_2–) is also observed. The S-H stretching vibration at ca. 2580 cm^{-1} was very weak although visible in the sample functionalized in CO_2. The broad band centered at ca. 3450 cm^{-1} was assigned to the stretching vibration of surface silanols groups and the remaining adsorbed water. The bending mode of H-O-H was also observed at 1630 cm^{-1}. Absorption bands at 1220, 1080 cm^{-1} and 808 and 457 cm^{-1} are due to the asymmetric and symmetric Si–O stretching vibrations and Si–O–Si bending vibrations, respectively. [32-35] Similar FTIR spectra were obtained for the different samples.

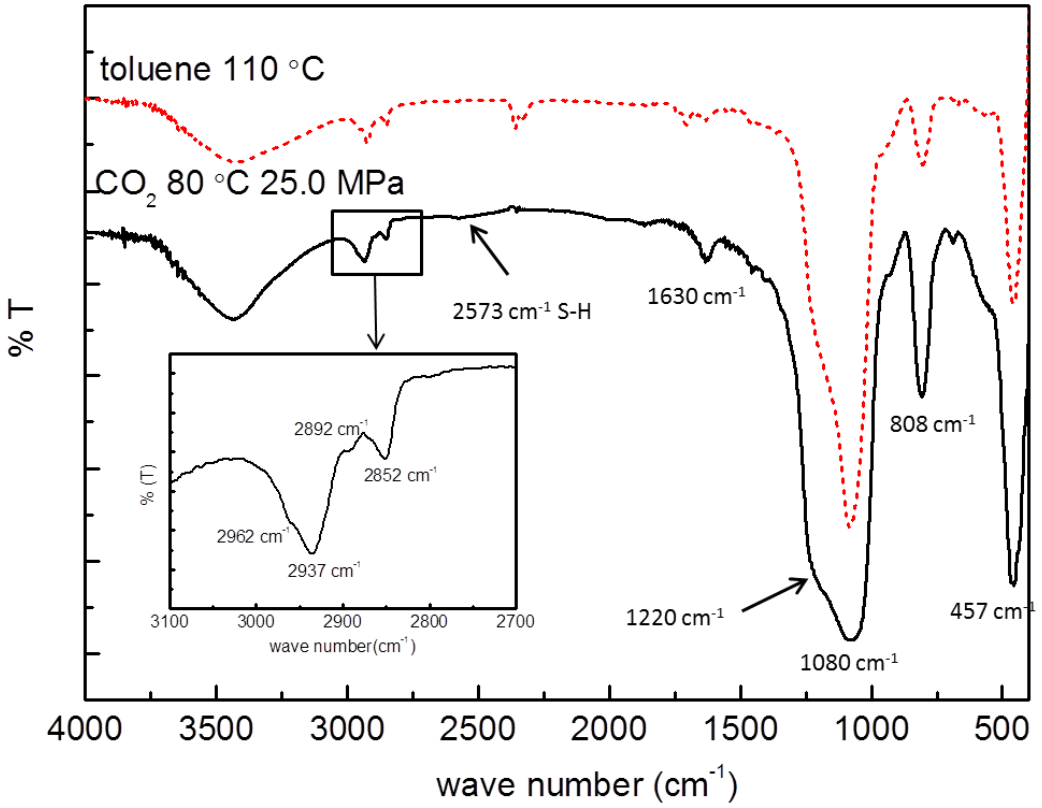

Figure 2- FTIR spectra of sample 6 functionalized in $scCO_2$ at 80 ºC and 25.0 MPa for 4 hours (—) and sample 13 functionalized in toluene at 110 ºC for 24 hours (·····).

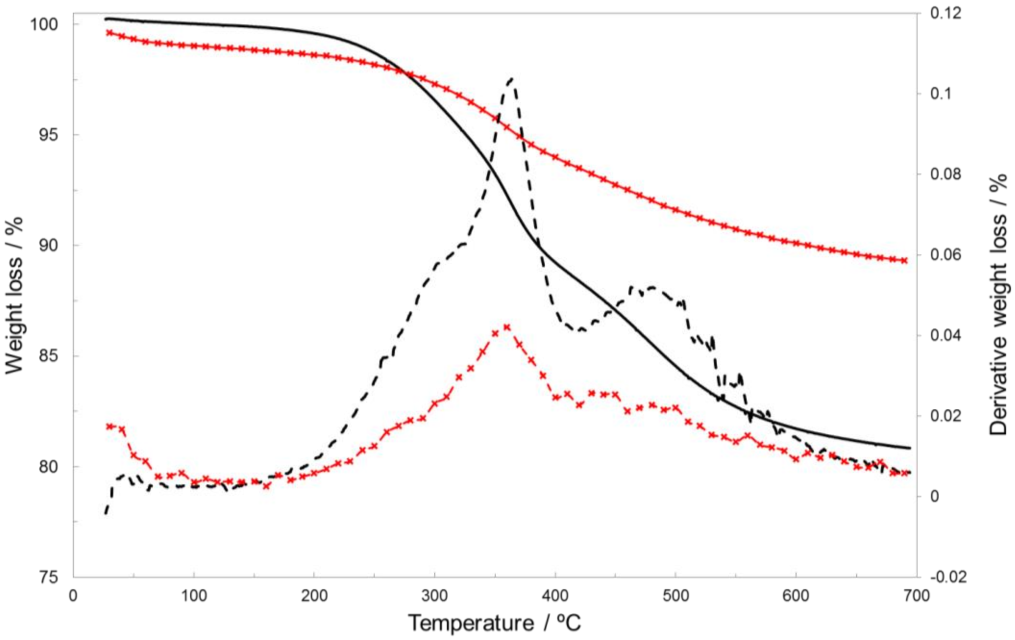

Figure 3 TGA of sample 6 functionalized in $scCO_2$ at 80 ºC and 25.0 MPa for 4 hours (—) and sample 13 functionalized in toluene at 110 ºC for 24 (✕) hours. Dash lines show the first derivative plotted as a function of temperature.

TGA analysis of sample 6 modified in $scCO_2$ at 80 ºC and 25.0 MPa and sample 13 modified in toluene at 110 ºC are given in Figure 3. Analysis revealed relatively large weight losses associated to the decomposition of the precursor. In both samples, several weight losses were observed at the following temperature intervals: 25-175, 175-310, 310-425 and 425-700 ºC. These intervals appeared in all the samples functionalized in $scCO_2$ and toluene. The weight loss below 175 ºC was ascribed to the loss of surface water and alcohol formed in the hydrolysis of the precursor. The weight loss in the 175-310 ºC range could be ascribed to the presence of unreacted precursor physically adsorbed on the SiO_2 surface. The weight loss in this interval was close to 3 or 4% for most samples prepared in $scCO_2$ and between 1 and 2% for the samples prepared in toluene. Weight losses above

310 ºC have been attributed to the thermal decomposition of the mercaptopropyl organic groups attached to the surface. The higher decomposition temperatures suggest covalent attachment of these groups to the surface.

Because decomposition or desorption of adsorbed MPTMS and derived physisorbed species and decomposition of covalent attached silanes are difficult to separate and following previous reports[26], the total amount of thiol groups on the surface was established from the mass percent loss between 175 and 700 ºC. Grafting densities (φ_m) in (mmol MPTMS/g SiO_2) were estimated assuming total hydrolysis of the precursor as

$$\varphi_m = \frac{\%\ \text{mass loss}\ (175 - 700\ °\text{C})/\ 75}{100 - \%\ \text{mass loss}\ (25 - 700\ °\text{C})}$$

where 75 g mol^{-1} is the molar mass of the organic part $-(CH_2)_3SH$. This value is an approximation, due to the presence of physisorbed species and the large number of possible partially hydrolyzed structures (Figure 1).

Surface coverage (φ_S) in (molecules nm^{-2}) was calculated for φ_m and the BET surface area of the support, S_{BET}, following

$$\varphi_S = \frac{\varphi_m\ \mathrm{N}_A}{S_{\text{BET}}}$$

Elemental analysis for the different samples is also provided in Table 1. C to S mass ratios ranged from 1.3 to 2.3 in all the samples. If complete hydrolysis of the precursor took place (forms D and F in Figure 1) a 3:1 C to S molar ratio would be expected (1.13 C to S mass ratio). On the other hand, if physical adsorption with no hydrolysis was taking place, a 6:1 C to S molar ratio (2.25 C:S mass ratio) would be observed. The fact that values in most cases are intermediate between the former situations suggests that hydrolysis is not complete.

Results for the different experiments performed in $scCO_2$ and toluene are given in Table 1. At 60 ºC and 15.0 MPa, reaction time was varied from 1 to 4 h. C:S mass ratios were at these conditions very high, indicating incomplete hydrolysis of the reactants. Grafting density increased as reaction time increased from 1 to 2 hours, but it decreased slightly for 4 hours. However, considering that the lowest C:S mass values were obtained at 4 h, in the following experiments the reaction time was fixed to 4 h. At 60ºC, the pressure was then increased from 15.0 to 25.0 MPa and CO_2 density increased up to 0.787 g cm^{-3}. This pressure rise did not lead to substantial variations in the grafting density and C:S mass ratio. Therefore, the pressure effect is not significant at this temperature. At 25.0 MPa, temperature was also decreased at 40 ºC (CO_2 density 0.879 g cm^{-3}) leading to similar grafting densities. Although temperature in this case was much lower, grafting density remained almost constant showing how the higher pressure and higher CO_2 density have a positive effect on the surface modification.

Next, temperature was increased up to 80 ºC, keeping the pressure constant at 25.0 MPa for 4 h, leading to a grafting density close to 2.3 mmol g^{-1}, whilst C:S mass ratio increased slightly to 1.6. At a longer time, 8 hours, grafting density increased to 3.1 mmol $g^{-1}$and C:S mass ratio decreased to 1.3. A further experiment at 100 ºC and 25.0 MPa was also performed. At these conditions, grafting densities and C:S mass ratios were similar to those obtained at 80 ºC, which could be related to the lower density of the CO_2 mixture.

A few experiments were performed in the stirred reactor (samples 9 – 11). Grafting densities in this case were always larger than those corresponding to the samples obtained in the small reactor without stirring at the same experimental conditions. For example at 80ºC and 25.0 MPa, the grafting density at 4 hours reached a value of 3.5 mmol g^{-1} that was even larger than the value obtained at the same pressure and temperature conditions without stirring after 8 hours. Similarly, comparison of samples 8 and 10 at 100 ºC and 25 MPa showed that a larger grafting density was obtained with stirring. A slight decrease of the grafting density was observed at 25.0 MPa when temperature increased from 80 to 100 ºC. The maximum grafting density of 4.4 mmol g^{-1} was obtained at 150 ºC and 29.0 MPa. C:S mass ratios for samples 9 to 11 were 1.1, 1.7 and 1.4 at 80, 100 and 150 ºC, respectively. The C:S mass value for the sample prepared at 80 ºC suggested complete hydrolysis of MPTMS.

The experiments performed in $scCO_2$ show that grafting density increases with temperature, pressure, CO_2 density, time and stirring. The fact that grafting density increases with temperature clearly shows that the surface reaction is an activated process. Although solubility of MPTMS in $scCO_2$ is very high, pressure and CO_2 density also have a positive effect on the process probably helping in the dissolution process. The diffusion of the reactant to the support is also favored with increasing time and stirring.

For the experiments performed using the conventional method in toluene for 24 h, grafting density also increased with temperature from 80 to 110 ºC, whilst the C:S mass ratio decreased. However, even at 110 ºC, the grafting density was by far much lower than those obtained by functionalization in $scCO_2$ at much lower temperatures. Furthermore, from a green chemistry viewpoint, reaction in $scCO_2$ is much cleaner than that in toluene. These results demonstrate the advantages of using supercritical CO_2 as a functionalization medium.

Considering the maximum concentration of silanol groups[30], surface coverages between 3.7 and 1.2 molecules nm^{-2} were expected. These values correspond to the completely and partially hydrolyzed and condensed forms of MPTMS on SiO_2 (structures E and A in Figure 1, respectively). Feng *et al*. [34] have reported slightly larger surface coverages of 5.0 molecules nm^{-2} for a mesoporous SiO_2 material. The values calculated in this work are between 1.3 and 4.0 molecules nm^{-2} in agreement with the previous estimates.

N_2-adsorption-desorption isotherms were measured on the different samples. Figure 4 compares the adsorption-desorption isotherms of the bare support and the samples modified in $scCO_2$ at 40, 80 and 100 ºC and 25.0 MPa. All the isotherms exhibited a type IV with H1 hysteresis loop characteristic of highly ordered mesoporous materials with a well-defined cylindrical pore morphology. Upon functionalization isotherms shifted downwards, due to the decrease in surface area. Values for the BET surface area (S_{BET}) and total pore volume (V_P) of the different samples are given in Table 2.

Values for the surface area of the bare SiO_2 support samples were 592 and 674 m^2 g^{-1}. The highest surface area among the functionalized samples was measured for the sample prepared in toluene at 110 ºC, due to its lower grafting density (394 m^2 g^{-1}). S_{BET} for samples modified in $scCO_2$ at 40, 80 and 100 ºC and 25.0 MPa for 4 hours without stirring (samples 5,6 and 8) was much lower adopting values equal to 296, 245 and 221 m^2 g^{-1}, respectively. Surface area also decreased as the reaction time increased (sample 7). The larger the grafing density, the lower the surface area. S_{BET} for samples 9-11 modified using the stirred reactor were much smaller in agreement to their higher grafting densities. In particular sample 11, with the highest grafting density had a surface area of only 11 m^2/g, which limits the applications of this material.

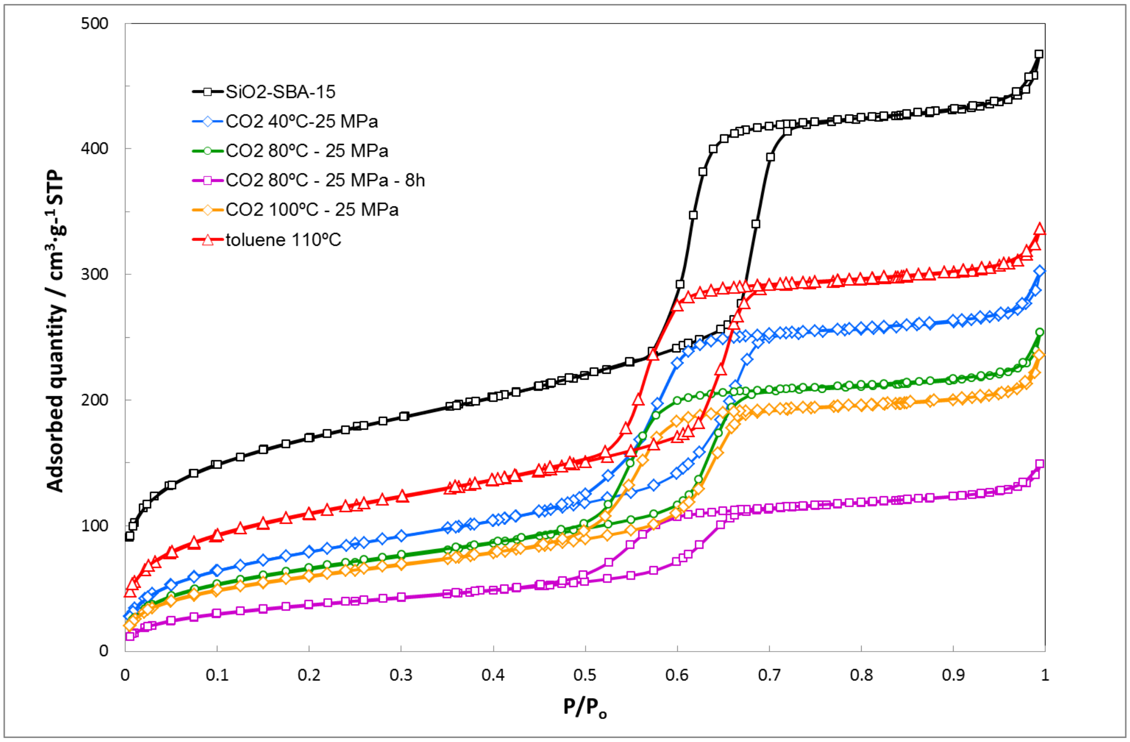

Figure 4- N_2 adsorption-desorption isotherms of bare SiO_2 SBA-15, samples functionalized in $scCO_2$ at different temperatures and reaction times (samples 5 to 8) and sample 13, functionalized in toluene at 110 ºC.

Similar variations with grafting density were observed for the total pore volume. V_P decreased from 0.73 $cm^3\ g^{-1}$ for the SiO_2 SBA-15 support to 0.230 $cm^3\ g^{-1}$ for sample 7 and 0.034 cm^3 g^{-1} for sample 11. The mesoporous support also presented a small micropore volume of 0.11-0.12 cm^3 g^{-1}, which disappeared completely with grafting, indicating filling of the micropores. Figure 4 shows how capillary condensation shifted gradually towards lower P/P_o values due to the lower mesopore size and the disappearance of the micropores.[36, 37]

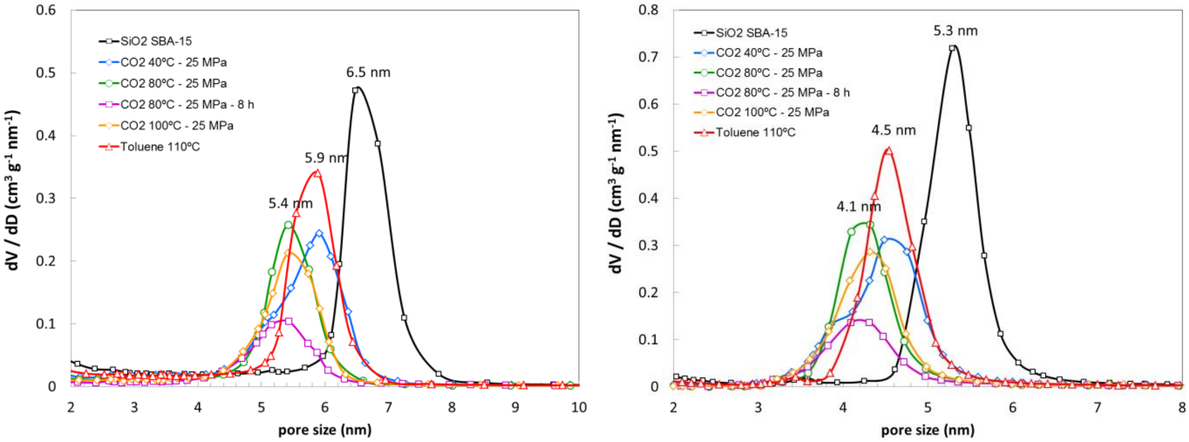

Figure 5- Pore size distributions obtained from the adsorption (left) and desorption (right) branches of the isotherms of bare SiO_2 SBA-15, samples functionalized in $scCO_2$ at different temperature, precursor concentration and reaction time (samples 5 to 8) and sample 13 functionalized in toluene at 110 ºC.

The pore size distributions of the adsorption and desorption branches of the isotherms were studied using the BJH method for a cylindrical pore model and are shown in Figure 5. For the bare SiO_2 SBA-15 support, pore sizes of 6.5 nm and 7.0 nm were obtained from the adsorption branch of the isotherm for the two samples used. Pore sizes of the functionalized samples were always lower than those of their bare supports and also peaks heights decreased substantially, which indicated modification of the internal surface of the cylindrical mesopores. The decrease in the pore size was lower for the sample modified in toluene at 110 ºC. Surprisingly, the pore size in the samples functionalized in $scCO_2$ decreased as the grafting density increased up to 5.4 nm (adsorption) at 80 ºC and 25.0 MPa. A further increase in the grafting density did not lead to a lower pore size, but to a decrease of the pore volume.

These results suggests the formation of a compact monolayer in the SiO_2 surface at temperatures over 80 ºC, as it has been previously reported by other authors.[25] For a theoretical length of the rest $O–Si-(CH_2)_3-SH$ equal to *ca.* 0.61 nm (estimated from the bond lengths and angles optimized using Hyperchem™ 7.1 software and the semiempirical method AM1) the formation of a compact monolayer would decrease the mesopore size by twice this amount, rendering a pore size of *ca.* 5.3 nm, which is just slightly lower than the pore size obtained. Upon increasing the temperature from 80 to 100 ºC or the time, the surface area and the pore volume decreased, suggesting partial clogging of some of the pores which are not accessible to the N_2 molecules.

Therefore, the best materials are those exhibiting large grafting densities and high surface areas with a pore size corresponding to the compact monolayer. Considering all the properties simultaneously, sample 6 reacted in $scCO_2$ at 80ºC and 25 MPa for 4 hours without stirring exhibited the best properties: high surface coverage and the highest surface area.

The low-angle XRD pattern of sample 6 was compared to that of the bare support (Supplementary data). Peak position did not change significantly after functionalization and demonstrates that the support structure is not altered with the surface modification in $scCO_2$.

There are previous reports on the surface functionalization of silica base materials with MPTMS using supercritical CO_2. Shin et al. [23] reported grating densities of 0.87 mmol g^{-1} zeolite for commercial zeolite beta of S_{BET} similar to SiO_2 SBA-15 although exhibiting microporous structure. Functionalization was performed in $scCO_2$ at 150 ºC and 52 MPa for 12 hours. The much lower grafting density reported for this material could be related to the microporous structure of the support. On the other hand, Zemanian et al. [24] reported at the same temperature and pressure but much shorter time (0.5 hours) a maximum surface coverage of 6.44 molecules nm^{-2} on hydrated SiO_2 MCM-41. Although this value is larger than the maximum value of 4.0 molecules nm^{-2} obtained in this work at 150 ºC and 29.0 MPa using the stirred reactor, the gas adsorption properties of the material after modification were not reported. Ashu-Arrah et al. [26] carried out the modification of silica stationary phases in $scCO_2$. A maximum surface coverage equal to 3.04 μmol m^{-2} (1.83 molecules nm^{-2}) was obtained at 70 ºC and 41.4 MPa for 1 h with stirring. This value is much lower than the measured in our work at a similar temperature. They also reported a decrease in the surface coverage at temperatures above 70 ºC and times longer than one hour.

The sometimes unclear procedure employed in the determination of the surface coverage in the different publications and the lack of the material structural characterization after modification make difficult the direct comparison. However, it seems clear that lower temperature and pressures conditions than those previously employed can be applied to the process. All these reports demonstrate that silylation in $scCO_2$ is a clean, fast and efficient route for SiO_2 surface functionalization. Our study also demonstrates how microstructural parameters should be taken into account to evaluate the success of the functionalization procedure.

Table 1 Summary of the surface functionalization experiments in $scCO_2$ and toluene at several temperatures, pressures and reaction times showing the weight loss at the different temperature intervals, grafting density (φ_m), surface coverage (φ_s), C:S mass ratio from microanalysis results and density of $scCO_2$. [38]

Sample #	***T* (°C)**	***P* (MPa)**	***time* (h)**	**Weight loss (%)**				**φ_m (mmol g^{-1})**	**φ_s (molecules nm^{-2})**	**C:S mass ratio**	**$\rho\,CO_2$ (g·cm^{-3})**
				25-175°C	**175-310°C**	**310-435 °C**	**425-700 °C**				
1	60	15.0	1	1.7	2.9	2.4	3.2	1.3	1.3	2.0	0.604
2	60	15.0	2	18	3.1	3.6	4	2.0	2.0	2.2	0.604
3	60	15.0	4	3.3	3.1	3.9	3.8	1.7	1.7	1.7	0.604
4	60	25.0	4	8	2.6	3.1	4.1	1.6	1.6	1.6	0.787
5	40	25.0	4	1.9	2.9	3.7	4.4	1.7	1.7	1.4	0.879
6	80	25.0	4	0.9	3.8	5	5.9	2.3	2.4	1.6	0.686
7	80	25.0	8	0.5	4.8	6.7	7.4	3.1	2.8	1.3	0.686
8	100	25.0	4	1	2.9	5.5	5.9	2.3	2.3	1.2	0.588
9ǂ	80	25.0	4	0.6	5.2	7.8	7.8	3.5	3.2	1.1	0.686
10ǂ	100	25.0	4	0.6	4.6	7.5	6	3.0	2.7	1.7	0.588
11ǂ	150	29.0	4	0.4	1.8	13.1	10	4.4	4.0	1.4	0.478
12	80	Toluene	24	1	1.1	1.4	1.5	0.6	0.6	2.3	-
13	110	Toluene	24	1	1.7	3.5	4.3	1.4	1.4	1.6	-

ǂ Experiments performed in the stirred reactor.

Table 2- N_2-adsorption desorption isotherm data for the SiO_2 SBA-15 support and the modified samples showing the BET surface area (S_{BET}), the total pore volume (V_P) and the pore size.

Sample #	S_{BET}(m^2/g)		V_P (cm^3/g)		Pore size (nm)	
	Support	Sample	Support	Sample	Support	Sample
4	592	256	0.735	0.398	6.5	5.5
5	592	296	0.735	0.468	6.5	5.9
6	592	245	0.735	0.393	6.5	5.4
7	674	137	0.733	0.230	7.0	5.4
8	592	221	0.735	0.365	6.5	5.4
9	674	85	0.733	0.159	7.0	5.7
10	674	216	0.733	0.361	7.0	5.7
11	674	11	0.733	0.034	7.0	–
13	592	394	0.735	0.365	6.5	5.9

4. CONCLUSIONS

Functionalization of SiO_2 SBA-15 with MPTMS has been successfully carried out in $scCO_2$ at 40-150 ºC and 25.0-29.0 MPa for 1-8 hours. The precursor solubility data in $scCO_2$ were considered so that moderate conditions for complete miscibility of both components were chosen. The grafting density and surface coverage increased with temperature, CO_2 density, reaction time and stirring. A compromise must be reached for temperature and pressure. Higher temperatures favor an activated process but lead to a lower CO_2 density at a given pressure and make less effective the supercritical medium.

Values for grafting density and surface coverage in $scCO_2$ were much larger than those obtained refluxing toluene at 110 ºC after 24 hours. This seems to be due to the better transport properties of $scCO_2$ which allow the fast penetration and diffusion of the reactant into the support pores. Furthermore, functionalization using $scCO_2$ can be considered a sustainable process. Microstructural characterization by gas adsorption showed how surface area and pore volume decreased as the grafting density increased. Pore size also decreased up to the formation of a compact monolayer. Further increase in the grafting density led to pore blocking and a substantial reduction of the surface area. Sample 8 prepared at 150 ºC and 29.0 MPa with stirring led to the highest grafting density (4.4 mmol g^{-1}) and surface coverage (4.0 molecules nm^{-2}) but with almost complete pore blockage, which led to very low surface area and pore volume. Sample 6 synthesized at 80 ºC, 25.0 MPa and 4 hours without stirring exhibited the best properties: high surface coverage and high surface area and pore volume. Shorter times can be employed if stirring is incorporated. In comparison to previous reports on the surface modification of other porous SiO_2 supports in $scCO_2$, the reaction was performed at lower temperature and/or pressure conditions. It is also shown that microstructure must be always taken into account in the functionalization process to maximize the material efficiency.

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SUPPLEMENTARY INFORMATION

THIOL GROUP FUNCTIONALIZATION OF MESOPOROUS SiO_2 SBA-15 USING SUPERCRITICAL CO_2

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Figure S1 compares the low angle XRD patterns of the SiO_2 SBA-15 substrate and sample 6 modified with mercaptopropyltrimethoxysilane (MPTMS) dissolved in supercritical CO_2 ($scCO_2$) at 80 ºC and 25.0 MPa for 4 hours.

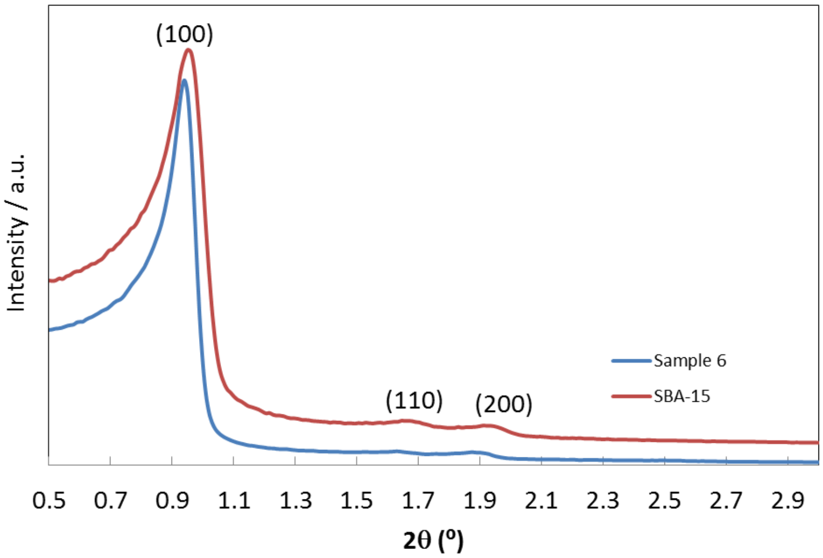

Figure S1. Low angle XRD patterns of SiO_2 SBA-15 support and sample 6 modified in $scCO_2$.

XRD patterns showed three well resolved peaks which were indexed according to the two dimensional *P6m* hexagonal symmetry. The first peak was assigned to the (100) planes and appeared at ca. 0.94 2θ values for the SiO_2 SBA-15 support. Values of 9.2 and 10.7 nm were calculated, respectively, for the spacing between (100) planes, d_{100}, and the cell parameter, a_o, corresponding to the distance between two pores centers. The slight difference in the peak position for the two samples is within the experimental error. We conclude that the modification process in $scCO_2$ does not alter the support structure.