

Materials for CO₂ capture prepared using supercritical CO₂

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ABSTRACT

Our work examines the concurrent use of scCO₂ technology for different processes intensification, including the efficient carbonation of calcium oxides and the deposition of amines in porous adsorbents. For these processes, the use of sonochemistry with supercritical CO₂ appears as a non-conventional promising technique adequate for increasing the efficiency in materials processing.

Mineral carbonation is one of the major processes in the long-term global carbon cycle and it is widely investigated in the frame of industrial carbon sequestration. Moreover, precipitated calcium carbonate (PCC) is widely used in different fields of industry. PCC is conventionally produced through the gas(CO₂)-solid(Ca(OH)₂)-liquid(H₂O) carbonation route, although this process is slow with low yield. The ultrasounds-supercritical developed method for PCC formation can be used for designing continuous processes, since the carbonation kinetics are significantly accelerated (from hours to minutes) with respect to the conventional batch process. The developed technology could also contribute to understand processes of accelerated ex-situ mineral CO₂ sequestration (controlled carbonation in industrial reactors of natural rocks or alkaline industrial waste) aimed at contributing to reduce the CO₂ emissions.

This work also aims at developing a generic supercritical silanization method into porous substrates using scCO₂ as a solvent. Different micro and mesoporous silica compounds were studied. First, hydrophobic silanes were used to impregnate the internal surface of the chosen substrates to obtain high capacity oil adsorbents. Second, preliminary experiments were performed to tailor the surface of porous silica compounds by coating with different aminosilanes, improving its potential for CO₂ capture. Results showed the efficiency of the supercritical method to load a large amount of silane compounds into the pores of the substrate without blocking the interconnected porous structure.

Key words: sonochemistry, carbonation, silanization, aminosilanes, porous materials

INTRODUCTION

The removal of anthropogenic CO₂ from combustion processes has been spotlighted in recent years as a potential way to reduce greenhouse gas emissions in industries. Among a range of proposed separation technologies, including membrane separation, absorption, cryogenic distillation, and others, the sorption with solids (activated carbons, zeolites, calcium oxides or hydrotalcites) appears to be one of the most promising alternative. Adsorption processes for gas separation via selective adsorption on solid media are widely used nowadays [1]. These adsorbents can operate via weak physisorption processes or strong chemisorption interactions. Solid adsorbents are typically employed in cyclic, multimodule

processes of adsorption and desorption, with desorption induced by a pressure or temperature swing.

The CO₂ capture process from combustion flue gases using CaO as regenerable sorbent was originally proposed by Shimizu *et al.* [2] 20 years ago. This emerging technology involves the separation of CO₂ using the reversible carbonation reaction of CaO to capture CO₂ from the flue gas and the calcination of produced CaCO₃ to regenerate the sorbent and to produce concentrate CO₂. The carbonation-calcination cycle is under consideration for practical large scale post-combustion applications. In general, both CO₂ sorption kinetics and calcium-based mineral absorption capacity increase to a considerable extent by decreasing mineral particle size to submicronic sizes. On the other hand calcium-oxide, based adsorbents suffer from a rapid degradation of CO₂ capture capability during the repetition of carbonation/calcination cycles, mainly attributed to pore blocking and adsorbent sintering. In light of this, extensive efforts have been made to enhance the stability of particulate systems by modifying the precursor properties, specifically with a focus on increasing surface area while preparing a more stable pore structure. The main studied strategies have been the use of rigid supports, the use of additives, the synthesis of nanoparticles and the use of different synthetic precursors.

On the other hand, the current benchmark technology being considered for post-combustion CO₂ capture is absorption by aqueous solutions of amines (e.g., monoethanol amine). For this applications, the immobilization of aqueous amines onto a solid support (e.g., porous silica) could have several advantages related with the reduction of amine degradation due to evaporation during the CO₂ recovering step. Silica supported amines were first used for CO₂ capture by Tsuda in 1992 [3]. There are two main classes of materials; amines covalently bound to the silica support, and amines physically impregnated into the silica support pore space.

The preparation of of these two types of solid adsorbents (calcium oxides and hybrids) using scCO₂ technology are described in this article. In the first part, results obtained for the accelerated scCO₂ carbonation of concentrated slurries and wet (CO₂ water saturated) samples of calcium hydroxide (Ca(OH)₂) using different agitation methods are presented [4-9]. In the second part, results showed the efficiency of the supercritical method to load a large amount of silane compounds into the pores of mesoporous substrates without blocking the interconnected porous structure [10-13]. The aim of this on-going work is the impregnation of silica substrates with aminosilanes using scCO₂ technology. In both cases, the application of ultrasonic agitation represents an efficient way of enhancing mass transfer.

MATERIALS AND METHODS

Materials

Ca(OH)₂ and CaO were purchased from Merck. Octyltriethoxysilane and (3-(2-aminoethylamino)propyl)trimethoxysilane from Fluka were the studied silanes. Mesoporous silica gel was used as the porous adsorbent. CO₂ (99.995 %) was supplied by Carburos Metálicos S.A. (Spain).

Equipment and procedure

Carbonation experiments: Fig. 1a shows a schematic drawing of the high-pressure apparatus used for carbonation. Experiments were carried out in a 110 mL reactor (Autoclave Engineer) operated in batch mode at 130 bar. The reactor was charged with a solid Ca²⁺-source and water in two different configurations. In the first design (Configuration 1),

suspensions of $\text{Ca}(\text{OH})_2$ (200 gL^{-1}) or CaO (151 gL^{-1}) in water were added to the reactor up to a filling level of 9 vol% (10 mL). In the second set of experiments (Configuration 2), the Ca^{2+} source and the liquid phase were placed physically separated in the reactor: 1 g of dry solid CaO was placed at the bottom of the vessel and a small amount of water (0.5 mL) was sprinkled on cotton wool placed in the middle of the reactor. In this configuration, the CO_2 added to the system was expected to flow through the cotton-wool supporting the water and to dissolve the water until saturation. The effect of the stirring method was studied using three different set ups: the first series of experiments was performed without agitation (na), the second one with vertical mechanical stirring (vm, 300 rpm) and the third one with ultrasonic agitation (us, 42 kHz and 70 W). Once sealed, the vessel was heated to $40 \text{ }^\circ\text{C}$ and CO_2 was added until reaching 140 bar to start the carbonation reaction. After allowing the reagents to react for a maximum of 60 min, the reactor was depressurized rapidly and the suspensions recovered at this stage were filtered and dried under vacuum at $50 \text{ }^\circ\text{C}$.

Silanization experiments: The supercritical silanization of silica substrates was performed using the set-up depicted in Fig. 1b running in the batch mode. A high-pressure autoclave (TharDesign) with a volume of 100 mL, was used. The reactor was charged with *ca.* 0.5 g of substrate placed in the upper part of the autoclave in a metallic support. Liquid silane (*ca.* 0.5 mL) was added to the bottom of the reactor. Liquefied CO_2 was compressed by a syringe pump at the desired pressure. The autoclave was heated at the chosen temperature value using electric resistances. The system was stirred at 300 rpm with a magnetic stirrer. At the end of each experiment, samples were washed with a continuous flow of scCO_2 at 10 MPa and 318 K during 30 min to remove the excess of deposited silane.

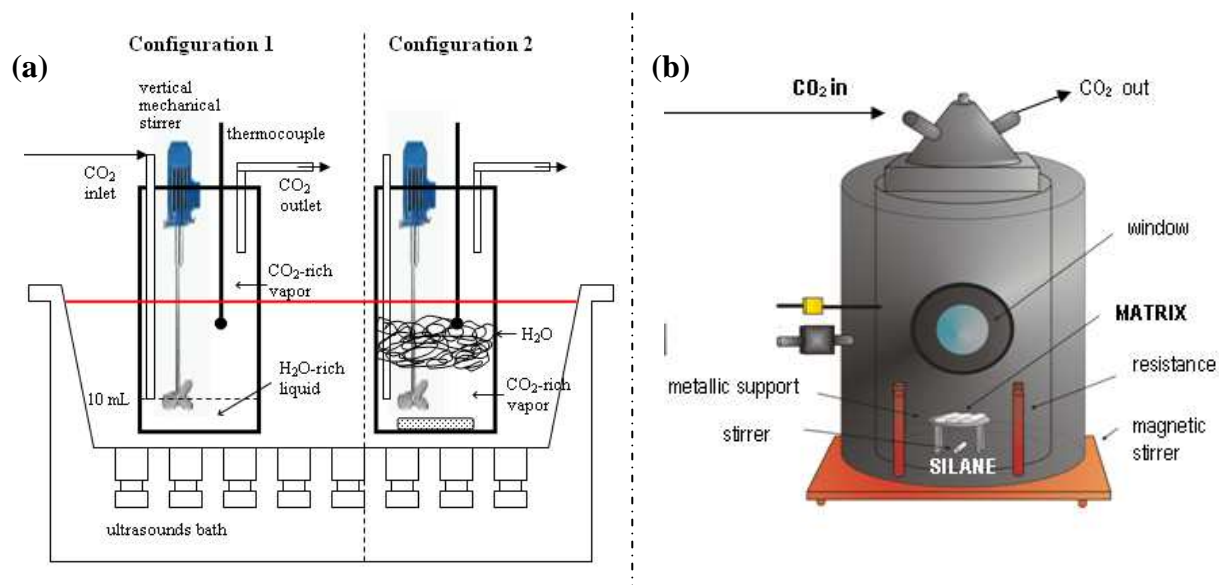


Figure 1. Schematic diagram of (a) the experimental apparatus used for the carbonation reaction describing Configurations 1 and 2; and (b) high-pressure equipment designed for batch supercritical silanization.

Characterization

The precipitated powder was analyzed by XRD with a Rigaku Rotaflex RU200 B instrument. The diffraction patterns were recorded from $2\theta = 20$ to 60° with a step scan of 0.02° counting for 1 s at each step. X-ray diffractometry was used to identify the relevant

calcium phases (CaCO_3 and $\text{Ca}(\text{OH})_2$ or CaO). These phases were, then, quantified by using the relative intensity ratio (RIR) method described elsewhere [7].

To confirm the presence of the coupling agent in the treated materials, Fourier transformed infrared (FTIR) spectra were recorded on a Perkin-Elmer Spectrum One instrument. Thermogravimetric analysis (TGA) of the modified silicas was performed in Ar using a TGA PerkinElmer 7. Textural characteristics of blank and silanized SiO_2 substrates were studied by low-temperature N_2 adsorption-desorption analysis (ASAP 2000 Micromeritics). Prior to measurements, samples were dried at $150\text{ }^\circ\text{C}$ during 48 h. Weight loss data from the TGA of treated materials and specific surface area of blank substrates were used to further estimate the number of silane molecules per nm^2 on the surface of the treated matrices. The adsorbed water content before and after silane treatment of the silica gel was measured using the Karl Fischer method. Silica porous samples were exposed to a relative humidity of 95 % at $21\text{ }^\circ\text{C}$ during 30 days. The adsorbed water content was measured using a 633 Karl Fischer-Automat (Methrom AG, Zofingen, Switzerland equipped with a 715 Dosimat burette and a 703 Ti Stand stirrer, using anhydrous methanol and the Karl Fischer's reagent.

RESULTS AND DISCUSSION

Carbonation reaction in scCO_2

The study of the rate of carbonation of concentrated slurries of $\text{Ca}(\text{OH})_2$ was performed using Configuration 1 (Fig. 1a) by allowing the reagents to react between 5 and 60 min. The diffractograms of all the precipitated samples revealed the presence of the representative peaks of both $\text{Ca}(\text{OH})_2$ and CaCO_3 , indicating incomplete calcium hydroxide conversion. The degree of $\text{Ca}(\text{OH})_2$ conversion to CaCO_3 for each performed experiment is represented in Fig. 2, where the line at the initial reaction stage indicated the constant carbonation rate (CCR) period, while the second one indicated the falling carbonation rate (FCR) period.

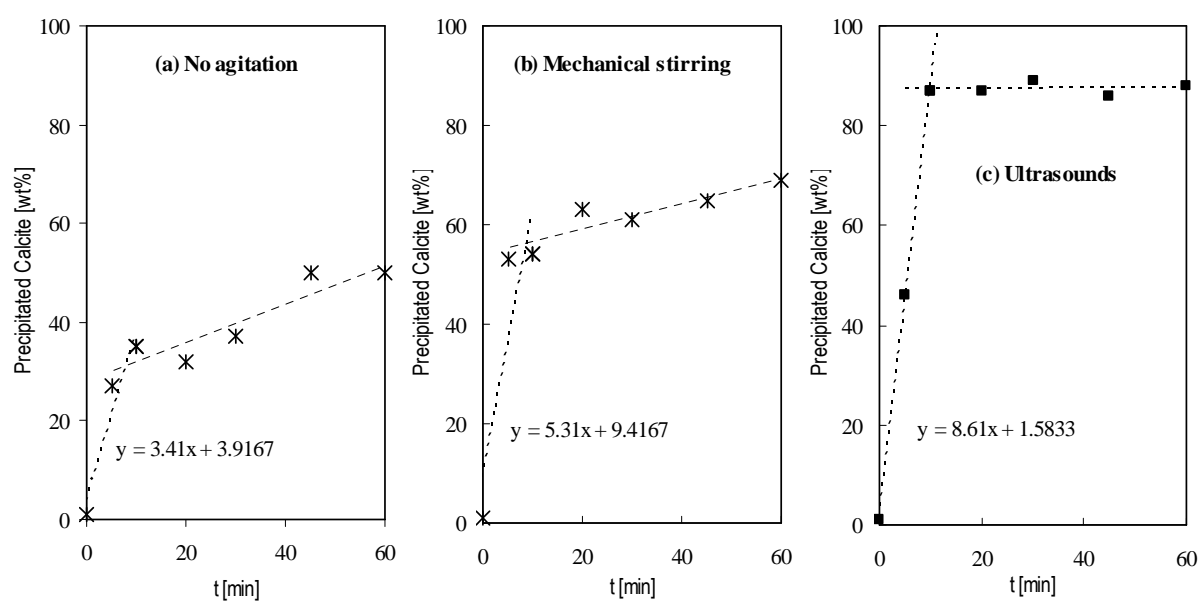


Figure 2. Experimental conversion data for a slurry of $\text{Ca}(\text{OH})_2$ /water (200 gmL^{-1}) using Configuration 1 in (a) no agitation, (b) mechanically stirred and (c) ultrasounds treated samples.

The duration of the CCR periods, determined by the interception of the two lines for each system, were of *ca.* 6-10 min for the three systems. At this time, around 32, 55 and 87 wt% of carbonation yield were achieved for the na, vm and us systems. In the studied carbonation process, both the kinetics and the conversion degree were influenced by the stirring efficiency. Comparing the three systems, we observed that the slope (rate of conversion) of the CCR line was higher for the ultrasounds treated system (8.6 gmin^{-1} , Fig. 2c) than for the mechanically or non stirred systems (5.3 and 3.4 gmin^{-1} , Fig. 2b and 2a). Moreover, the ultrasounds were also clearly superior to mechanical stirring at large periods of carbonation, since the overall degree of conversion after 60 min was 85-90 % with ultrasonic agitation, and only 65-70 % with mechanical stirring.

In the experiments performed applying ultrasounds stirring, the main mechanism responsible of the high attained conversion was related to the intense agitation caused by acoustic streaming, and from the shearing forces, jets and shock waves produced by cavitation collapse in the water-rich phase. Moreover, applying ultrasonic agitation also causes significant mixing and turbulent motion in both the liquid phase and the suspended solids. Finally, collisions between growing crystals can produce abrasive surface effects and small fragments in the precipitated CaCO_3 (Fig. 3), which favor further dissolution of Ca(OH)_2 and enhance the diffusion of newly formed Ca^{2+} in the FCR stage of the reaction.

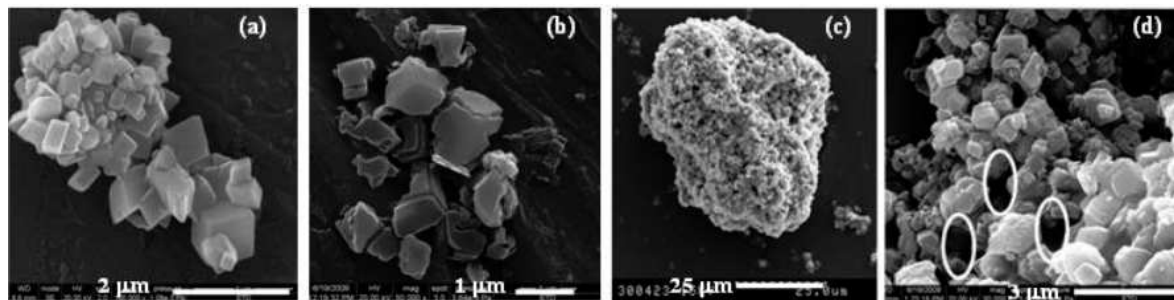


Figure 3. Precipitated CaCO_3 particles using (a) mechanical and (b,c,d) ultrasounds stirring (20 min) using Configuration 1.

Further experiments were performed with a system consisting in wet CO_2 and dry CaO , therefore, having in the reactor a fluid phase mostly composed by CO_2 (Configuration 2 in Fig. 1a). Hence, the solid was mostly in contact with a scCO_2 phase saturated with water, instead of a CO_2 -saturated water phase, as it was in the first series of experiments performed using Configuration 1. Morphological analysis indicated that in all cases rhombohedral submicrometric calcite particles were precipitated (Fig. 4).

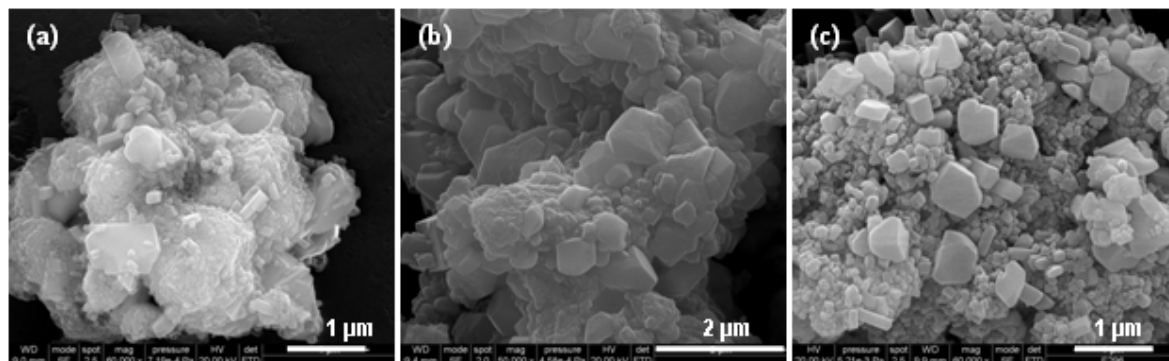


Figure 4. Precipitated calcite particles at 60 min originated from CaO using Configuration 2.

In media with a reduced amount of water, like the one used in experiments performed following Configuration 2, the interaction of the new nucleated tiny calcite particles with the substrate surface makes their interfacial free energy to decrease, thus, diminishing their tendency to grow and stabilizing the fine particles. Hence, a large population of nanometric particles (*ca.* 0.1-0.2 μm) was observed in the SEM images together with few micrometric crystals ($> 1 \mu\text{m}$).

Supercritical gas-liquid-solid and wet gas-solid systems were experimentally investigated in the precipitation process of calcium carbonate. In the two-phase fluid system, carbonation reaction took place in the liquid phase and both the conversion degree and the kinetics were highly influenced by the stirring method. The low conversion values obtained for the non-agitated samples indicated that the reaction kinetics was controlled by ions diffusion. On the contrary, for mechanically and ultrasounds stirred systems the high conversion values indicated predominant control of $\text{Ca}(\text{OH})_2$ dissolution at least in the first *fast* stage of the reaction. Due to the lack of a significant water-rich liquid phase when using scCO_2 containing dissolved water as the gas phase in contact with the solid precursor, the conversion values were less affected by the stirring method. Calcite with rhombohedral morphology was precipitated using both configurations. However, larger particles (1-3 μm) were obtained by carbonating slurries than by carbonating wet solid reagents, in which a nanometric system was precipitated. Moreover, strong CaCO_3 yield variations were found between the powders precipitated from either $\text{Ca}(\text{OH})_2$ or wet CaO in the gas-solid configuration. Under similar stirring conditions, the reactivity of wet CaO was higher than that of the slaked lime prepared using commercial dry $\text{Ca}(\text{OH})_2$.

Silanization reaction in scCO_2

The internal surface of micro and nanoporous substrates can be modified in terms of charge, functionality or even reactivity or stability by means of bifunctional organic molecules able to self-assembly. This work investigates the impregnation with trialkoxysilanes of porous systems using scCO_2 as a solvent, which combines several advantages such as liquid-like density and high solvating power with gas-like transport properties. Moreover, scCO_2 does not interact with the substrate and there is no competition for absorption between added reagents and solvent molecules. The work aims at describing a generic liquid-solventless impregnation method applicable to mesoporous (silica gels and agglomerated nanoparticles) silica-based substrates using scCO_2 . The hydrophobic octyltriethoxysilane was used to impregnate the internal surface of the chosen substrates with the objective of obtaining high capacity oil adsorbents.

Polar mesoporous substrates have a highly reactive surface with a hydroxyl surface density of 4-6 OHnm^{-2} . The mesoporous space facilitated the siloxane self-condensation reaction between adjacent silanols and the high hydroxyl surface density assisted the chemisorption, thus, resulting in highly stable coatings. For running times between 90 and 240 min, total mass losses for these materials were 5-6 wt%. The estimated grafting densities were *ca.* 0.85 silane molecules nm^{-2} . The acquired hydrophobic character was evaluated using the Karl Fischer method to measure the loss in water adsorption capacity after silane grafting. The water uptake was reduced by a 10-fold factor for mesoporous silanized materials.

Following a similar approach, we have tried to impregnate aminosilane molecules in the studied porous silica substrates. However, under working conditions, primary and secondary amines reacted directly with CO_2 to produce carbamates through the formation of zwitterionic intermediates. The mixture of amines and carbamates is a wax with null solubility in scCO_2 . Hence, before impregnation the experimental conditions must be

optimized for this system. The equilibrium amine/carbamate can be shifted mainly with temperature, although it is also influenced by pressure. To study the influence of these parameters, the aminosilane was pressurized with CO₂ at pressures between 8-16 MPa in a variable volume view cell (Figure 5). Initially a wax was formed until the temperature reached a value of *ca.* 393-400 K, where liquid amine was again visible. The optimal working pressure was 9-10 MPa.

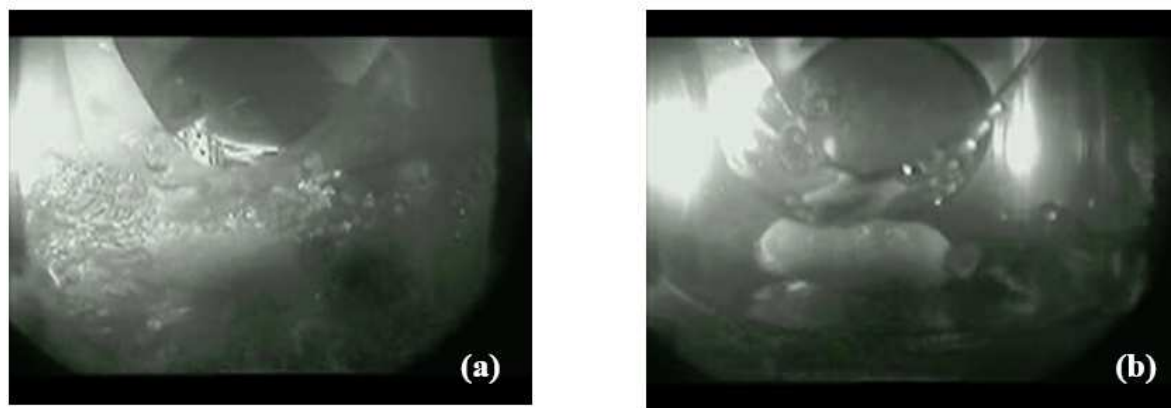


Figure 5. Equilibrium aminosilane/carbamate as a function of temperature: (a) wax observed at 348 K ($P = 12$ MPa), and (b) liquid aminosilane observed at 393 K ($P = 9$ MPa).

CONCLUSIONS

Experiments performed in this work under supercritical conditions, indicated that ultrasonic energy was effective in allowing CO₂ to access to the unreacted Ca(OH)₂ core, thus, enlarging the conversion grade. The main mechanism involved in the carbonation reaction improvement could be related with the intense agitation caused by acoustic streaming, and from the shearing forces, jets and shock waves produced by cavitation collapse in the liquid water phase.

The silanization of silica porous substrates with alkylsilanes in scCO₂ was also investigated. In contrast with conventional liquid solution-phase silanization, silanized porous substrates treated under scCO₂ preserved the porous character of the bare materials. The impregnation with aminosilane must be performed at high temperature (*ca.* 395 K) to moderate the formation of carbamates.

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