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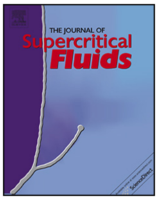

Regenerable solid CO_2 sorbents prepared by supercritical grafting of aminoalkoxysilane into low-cost mesoporous silica

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ABSTRACT

The present work examines the functionalization of silica supports *via* supercritical CO_2 grafting of aminosilanes, which is an important step in the preparation of materials used as solid sorbents in CO_2 capture. Four materials have been considered as solid supports: two commercially available silica gels (4.1 and 8.8 nm pore diameter), the mesoporous silica MCM-41 (3.8 nm pore diameter) and a microporous faujasite of the Y type. Mono- and di-aminotrialkoxysilane were chosen for this study. The optimal operating conditions required to have free aminosilane in solution were first evaluated by studying the phase behavior of the system $scCO_2$/aminosilane at different pressures and temperatures. FTIR spectroscopy was used to determine the chemical structure of the grafted species. Aminosilane uptake was estimated by thermogravimetric and elemental analysis. Densities up to 3–4 molecules of monoaminosilane per nm^{-2} were reached by using a small amount of a cosolvent together with the supercritical CO_2. The samples were characterized in regards of thermal stability, showing that aminosilane groups were covalently attached to the amorphous silica surface in the mesoporous supports, but not in the microporous zeolite. Low temperature N_2 and ambient temperature CO_2 isotherms were recorded to establish the adsorptive behavior of the prepared hybrid materials. The amine functionalized MCM-41 and the 8.8 nm silica gel exhibited a significant higher uptake of CO_2 at low pressures compared with the bare supports. On the contrary, for the 4 nm silica gel and the zeolite the adsorption decreased after impregnation.

1. Introduction

Carbon dioxide (CO_2) chemical absorption using aqueous alkanolmono and diamines is considered a benchmark mature technology for the separation of dilute combustion flue gases [1]. The use of solid porous sorbents modified with aminopolymers [2–4] or aminosilanes is now being widely considered as an alternative separation technology to alkanolamines, potentially less-energy-intensive [5–8]. The immobilization of aminosilanes on the internal surface of solid porous supports, typically porous silica producing aminosilica, has several advantages. Aqueous amines, including moderated evaporation and reduced degradation of amine during recycling. The synthesis of the aminosilica can be carried out either by co-condensation of the aminosilane with the silica source or by grafting aminoalkoxysilane molecules to the previously synthesized silica support [9–11]. The grafted compounds have an exceptional high thermal stability and are used for a large variety of applications, such as catalysis and adsorption, and as intermediates for advanced synthesis procedures [12,13].

The common grafting approach used for aminosilica synthesis involves a liquid-phase deposition step, being the traditional method admixing in toluene. However, this approach generates significant amounts of organic solvent waste. Moreover, oligomerization in solution is often a side reaction of the liquid deposition method, which negatively affects surface coverage homogeneity. Compared to liquid-phase methods, there have been relatively few reports on aminosilane gas-phase grafting, which embrace chemical vapor deposition (CVD) [14] and supercritical fluid impregnation [15]. The use of solvent less deposition routes, including CVD, has been limited to volatile and thermally stable aminosilanes grafted on flat surfaces [16]. In contrast, SCF anhydrous silanization using $scCO_2$ as a solvent has been shown as one of the most effective, simple and reproducible methods for producing homogeneous, covalently bonded, high density silane films on the internal surface of porous materials [17–20]. For the specific application of coating of nano and microporous supports, the use of $scCO_2$ as a solvent has the advantage of its gas-like diffusivity and zero surface tension, allowing the easy penetration of the fluid into the pores and the complete wetting of intricate geometries.

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Moreover, the waste stream inherent to the toluene preparation is eliminated, since the only byproducts of the $scCO_2$ process are CO_2 and alcohol, which can easily be separated and recycled.

Covalent bonding of organosilanes onto oxide supports using the supercritical method has been extensively scrutinized in the past in our laboratories. In previous studies, the supercritical silanization with alkyltrialkoxysilane of several micro and mesoporous silica supports was deeply analyzed [21,22]. On the basis of preceding results, the present work examines the functionalization of similar silica supports *via* supercritical silanization with aminosilanes. The process carried out for grafting aminosilanes to silica supports is complex, since it involves both the silane and the amine chemistry [23]. In addition, in the presence of compressed CO_2, primary and secondary alkylamines could react with the solvent to give nonsoluble carbamates [24,25]. Hence, an extensive study of process optimization in regards to working settings at supercritical conditions was performed prior to hybrid materials preparation.

Four different porous supports were examined in this work, including two different silica gels, mesoporous MCM-41 and microporous faujasite. All of them satisfy the key attributes required for inorganic supports to be used as solid sorbents: inertness, robustness over a wide range of pressure and temperature and easiness of functionalization. In addition, mesoporous silica gels have the advantage of being very low in cost. The supports were modified with 3-(methylamino)propyl and N-(2-aminoethyl)-3-aminopropyl trialkoxysilanes. The coating thermal stability and the surface coverage were determined using thermogravimetric analysis, corroborated by elemental analysis. The aminosilane–silica chemical interaction was studied by Fourier transformed infrared spectroscopy. Finally, the adsorption capacity of prepared materials was evaluated by low-temperature N_2 adsorption–desorption measurements, while the performance for CO_2 sorption was analyzed by recording CO_2 isotherms.

2. Materials and methods

2.1. Materials

3-(Methylamino)propyl (MAP) and N-(2-amino ethyl)-3-aminopropyltrimethoxysilanes (AEAP), both from Sigma–Aldrich, with 106 and 236–237 °C boiling points, respectively, were used as grafting solutes. Four different supports were scrutinized: silica gel cleancat (CC, Iberamigo S.A.), silica gel 40 (SG40, Fluka), mesoporous silica MCM-41 (MCM41, ACS Materials) and the aluminosilicate zeolite Y (ZY, Strem Chemicals). Samples CC and SG40 were dried in an air-oven at 120 °C overnight before use. The mesoporous MCM-41 was boiled in distilled water at 100 °C for 1 h [26] to increase the surface silanol density to 3 OH nm^{-2}. The microporous zeolite ZY was activated by calcination in a tubular oven (Carbolite 3216) at 520 °C during 48 h under a flow of nitrogen with oxygen traces. CO_2 (99.999%, Carburos Metálicos S.A.) was used as a solvent. Dry ethanol (Et), methanol (Mt) and Ether (Eth), obtained from Panreac, were used as cosolvents.

2.2. Selection of experimental conditions

The extent of mixing of the studied aminosilanes with CO_2 was essential information necessary to settle the operating conditions in the supercritical silanization process. For primary and secondary alkylaminosilanes, solubility in $scCO_2$ cannot be reported, since during the experimental determination they react with CO_2. Hence, only the qualitative behavior of the studied aminosilanes with temperature and pressure in $scCO_2$ could be ascertained. The performance was visually analyzed using a variable-volume cell (10 mL) with a sapphire window (Phase Equilibrium Analyzer, Thar Technologies Inc.). Compressed CO_2 (∼6 MPa) was introduced from a cylinder into the view cell previously heated at 45 °C, which contained 1 mL of aminosilane. The cell was then slowly heated to temperatures higher than 135 °C. The pressure inside the solubility cell was kept constant in the range 7.5–9.0 MPa, either by pumping more CO_2 or by relaxing gas excess. Phase transitions occurring with temperature were visually determined in a video output by observing the phase conditions in the cell with stirring.

2.3. Equipment and procedure

The supercritical silanization of silica substrates was performed using a set-up depicted elsewhere [21]. A high-pressure autoclave with a volume of 100 mL (Autoclave Engineers) was used for aminosilane deposition. The reactor was charged with *ca.* 0.3 g of substrate enclosed in a cylindrical cartridge made of 0.45 μm pore filter paper, which was placed in the upper part of the autoclave. Liquid aminosilane (*ca.* 1 mL) was added at the bottom of the reactor. Before the addition of compressed CO_2, the reactor was heated at 100 °C while applying a moderate vacuum during 20 min to eliminate water from the system. Experiments were performed in the batch mode by adding compressed CO_2 up to the desired pressure (P) once the equipment was heated at the chosen temperature (T). For experiments involving a cosolvent, a measured amount of Et, Mt or Eth (2–5%v) was added to the autoclave before CO_2 injection. Running time was of 300 min, keeping the stirring at 300 rpm. At the end of each experiment, the reactor was depressurized and led to cool to room temperature.

2.4. Characterization

To confirm the presence of the coupling agent in the treated materials, Fourier transformed infrared (FTIR) spectra of the recovered samples mixed with KBr were recorded on a Perkin-Elmer Spectrum One instrument. Thermogravimetric analysis (TGA) of the modified silica was performed under N_2 flow using a TGA Instrument Q5000 IR and at a heating rate of 10 °C min^{-1}. In some samples, organic elemental analysis of C, N and H were performed (Flash EA2000 Thermo Fisher Sci.). Textural characteristics and physisorption capacity of raw and silanized substrates were studied by low temperature N_2 adsorption–desorption analysis (ASAP 2000 Micromeritics). Prior to measurements, mesoporous substrates were dried under reduced pressure at 120 °C for 20 h. FTIR and TGA analysis of some selected samples were performed after N_2 adsorption characterization to verify that the standard degassing temperature of 120 °C did not modified the loading of the synthesized hybrid products. FTIR analysis indicated that the carbamate peaks disappeared from the synthesized samples by outgassing at 120 °C. Sample containing micropores (ZY) was dried at 150 °C during 48 h. The specific surface area (S_a) was determined by the BET method. The mesopore volume (P_v) was calculated using the BJH method from the adsorption branch of the isotherm, while the micropore volume (μP_v) was estimated by the *t*-curve method. Sorption isotherms of CO_2 were obtained using a Micromeritics ASAP 2020 analyzer in the interval 0–100 kPa. Prior to measurements, samples were outgassed under reduced pressure following the same procedure than for N_2 adsorption. A circulator bath containing heated oil was used to obtain the isotherms at different temperatures.

3. Results and discussion

The four different supports scrutinized in this work are schematized in Fig. 1a. Mesoporous CC, SG40 and MCM-41 are all constituted of amorphous silica, while the microporous zeolite Y is