



Production of silica aerogel microparticles loaded with ammonia borane by batch and semicontinuous supercritical drying techniques



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ABSTRACT

Silica aerogel microparticles were prepared by supercritical drying and used as support for hydrogen-storing ammonia borane (AB). The formation of aerogel microparticles was done using two different processes: batch supercritical fluid extraction and a semicontinuous drying process. Silica aerogel microparticles with a surface area ranging from 400 to 800 m²/g, a volume of pores of 1 cm³/g, and a mean particle diameter ranging from 12 to 27 μm were produced using the two drying techniques. The particle size distribution (PSD) of the microparticles was influenced by shear rate, amount of catalyst, hydrophilic–hydrophobic solvent ratio and hydrophobic surface modification. In particular, irregular aerogel particles were obtained from hydrophilic gels, while regular, spherical particles with smooth surfaces were obtained from hydrophobic gels. AB was loaded into silica aerogel microparticles in concentrations ranging from 1% till 5% wt. Hydrogen release kinetics from the hydride-loaded aerogel was analyzed with a volumetric cell at 80 °C. By stabilization of AB into the silica aerogel microparticles, an improvement of the release rate of hydrogen from AB was observed.

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1. Introduction

Aerogels show some extraordinary properties such as high specific area (500–1200 m²/g), high porosity (80–99.8%), low density (0.003 g/cm³), high thermal insulation (0.005 W/mK), and low dielectric constant (1–2) and index of refraction (1.05) [1]. These outstanding properties make them useful materials for several applications such as thermal insulation [2], filters to removal toxic compounds [3], or as supports for inorganic nanoparticles [4].

Silica alcogels can be produced by a hydrolysis–condensation sol–gel reaction using tetramethylortosilicate (TMOS) as a precursor, producing siloxane bonds, plus water as a by-product, as presented in reactions (1) and (2). Condensation reactions continue forming a three-dimensional network through a polymerization

reaction, producing a silica gel immersed in an alcoholic medium known as alcogel [5].



The drying of the alcogel is an essential step in order to preserve the microstructure of the material and key properties such as surface area or pore volume. Different techniques have been used to dry the alcogel, including atmospheric and freezing drying. Also, since supercritical carbon dioxide is completely miscible with many volatile organic solvents, supercritical drying with carbon dioxide has been employed by several authors because it prevents fractures caused by the capillary stresses in the vapor–liquid interface that are unavoidable with other processes [6].

Aerogels can be synthesized as monoliths or alternatively as microparticles. Aerogel microparticles are of great interest in applications in which the aerogel acts as carrier material of an active compound, because by the reduction of the aerogel particles size the intraparticle diffusion processes can be adjusted to the

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requirements of the product. Therefore, aerogel microparticles have been used in different applications, and particularly in biomedicine, for drug delivery or encapsulation of active compounds [7].

Aerogel microparticles can be obtained by milling of monoliths, but since milling can damage the pore structure of the aerogel, the development of methods for the direct production of aerogel microparticles is of interest. Alnaief and Smirnova [8] presented a new method to produce spherical aerogel microparticles with a controlled particle size distribution and a mean diameter ranging from 200 μm to 1.7 mm. This method was based on a sol–gel method. The gel phase was made of tetramethylorthosilicate as precursor, methanol as solvent, and aqueous ammonia and HCl solutions as catalysts, diluted in ethanol in order to obtain the desired density. By mechanical stirring, this gel phase was broken into small droplets and dispersed within a continuous phase formed by canola oil saturated with ethanol. After gelation of the dispersed phase took place, gel spheres were left overnight for aging and later dried by supercritical extraction using supercritical carbon dioxide to remove the solvent and oil, thus producing dry aerogel particles. Also, Montes et al. [9], compared two processes for the production of silica microparticles: a conventional batch aerogel drying process using supercritical ethanol, and a novel process consisting in a simultaneous sol–gel reaction and drying, based on the continuous injection of precursors into supercritical carbon dioxide. In both processes, silica microparticles with spherical morphology and amorphous nature were obtained. However, by the continuous process bigger particles, more hydrophilic and with almost no porosity were obtained.

Due to their controlled size, thermal stability, and capacity to host and stabilize particles of an active compound in their pore volume, silica aerogel microparticles can be promising carrier materials for different active compounds, like hydrides used as solid state hydrogen storage materials. In particular, ammonia borane (AB) is a promising chemical hydride due to its potential to store a significant amount of hydrogen (up to 19.6%wt), low molecular weight (30.7 g/mol) and stability and safety in handling [10,11]. For these reasons, it has been considered as a candidate for storing hydrogen as needed for the implementation of the “hydrogen economy” [12]. However, ammonia borane also presents some shortcomings that must be overcome before this material can be applied for hydrogen storage applications. First, there are thermodynamic limitations because high temperatures are required in order to decompose the material and release all the stored hydrogen. The thermal decomposition of AB above 70 °C has been studied [13–15] using volumetric measurements, which showed that 1.1 mol of hydrogen per mol of AB were released at temperatures below 120 °C and another 1.1 mol was released at higher temperatures. This limitation can be improved modifying the chemical composition of the mixture adding compounds to de-stabilize the hydride, thus reducing the thermodynamic stability and the temperature required to decompose it [16]. On the other hand, ammonia borane has kinetic limitations due to a too slow release of hydrogen. It is believed that reducing the dimensionality of crystalline AB when it is confined in the mesopores of silica scaffolds results in changes in thermal properties and hydrogen-releasing kinetics [17] shortening diffusion distances. Other approaches for speeding-up kinetics and decreasing the onset temperature of the reaction include the use of ionic liquids as solvents for ammonia borane, [18] or using catalysts of Ru, Co, Ni or Pd in order to accelerate the generation of hydrogen from the methanolysis of ammonia borane [19].

In this work, the synthesis of silica aerogel microparticles has been studied. Two different methodologies have been tested: a batch drying process and a semicontinuous spray process. The results of both techniques have been compared examining the

particle size, particle size distribution (PSD), textural properties (surface area and pore volume) and particle morphology. Next, silica aerogel microparticles have been used as vehicles for the incorporation of ammonia borane to apply it as a solid state hydrogen storage material. Since some hydrides are unstable in CO₂ atmosphere [20], and some contradictory results are presented regarding to the behavior of ammonia borane in CO₂ environment [21], as a previous step the stability of pure solid ammonia borane and ammonia borane dissolved in methanol during exposure to carbon dioxide has been analyzed. Ammonia borane-loaded aerogel microparticles have been produced by precipitation of ammonia borane inside the pores of the alcogel using two different methods: precipitation before supercritical aerogel drying, and conventional homogenization by mechanical milling. Finally, kinetics of hydrogen release from the resulting material have been analyzed employing a volumetric cell at 80 °C.

2. Experimental methods

2.1. Materials

Tetramethylorthosilicate (TMOS, 98.0% purity), trimethyl-ethoxylane (TMES, 98% purity), ammonium hydroxide (28.0–30.0% ammonia purity) and ammonia borane (AB, 97% purity) were supplied by Sigma–Aldrich. Methanol (99.8% purity), n-hexane (95% purity) and dichloromethane (98% purity) were purchased from Panreac. Carbon dioxide (99.95% purity) was purchased from Carburos Metálicos S.A.

2.2. Methods

2.2.1. Preparation of silica alcogels

Silica alcogel was produced by the standard sol–gel reaction used to synthesize aerogel monoliths, with a key modification of the process: hexane was added to the reaction mixture, acting as a hydrophobic phase that enables the dispersion of the alcogel into small droplets, which after drying lead to the production of aerogel microparticles, as described by Alnaief and Smirnova [8]. The process was carried out under strong mechanical agitation in order to allow a better dispersion of these droplets.

TMOS was used as a precursor and it was mixed with methanol, water and hexane with a molar ratio of 1 mol TMOS: 4.4 mol MeOH: 3.3 mol H₂O: 2.3/4.5/6.8 mol hexane. Mechanical stirring at 500, 600 or 700 rpm was applied using a two bladed axial stirrer (Caframo). After 10 min, 250 μL of ammonium hydroxide diluted with water, with a ratio of 0.04, 0.08 or 0.12 mol NH₄OH: 1 mol TMOS were added to the first solution as condensation catalyst. Then, the solution was stirred for two hours while the gelation of silica alcogel particles took place. After that, an aging period of the alcogel immersed in methanol for one day was allowed in order to strengthen its structure. These steps were performed at ambient conditions. The hydrophobic alcogels were prepared in the same way using TMES as precursor with a ratio TMOS:TMES 1:2 or 1:5, without variations in the proportion of the rest of reagents.

2.2.2. Drying of alcogel microparticles by batch supercritical fluid extraction

The apparatus used to produce aerogel microparticles by batch supercritical drying is shown in Fig. 1. It was designed and supplied by Eurotechnica (Hamburg, Germany). It comprises the following main components: a stainless steel CO₂ buffer vessel with a capacity of 100 mL, an extraction vessel of 85 mL with a magnetic stirrer, and two pumps: an air-driven pump used for loading CO₂ into the system, and a gear pump (Micropump 180 Series mod. GAH-T23) used to recirculate CO₂ through the system in order to improve the contact between the supercritical fluid and the organic solvent.

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