

DEVELOPMENT OF ENHANCED HYDROGEN STORAGE MATERIALS BY STABILIZATION OF HYDRIDE NANOPARTICLES IN AEROGELS

Ángel Martín*, Miriam Rueda, Luis Miguel Sanz-Moral

High Pressure Processes Group, Department of Chemical Engineering and Environmental Technology,
University of Valladolid

Doctor Mergelina s/n 47011 Valladolid (Spain)

fax: +34 983 184865, e-mail: mamaan@iq.uva.es

ABSTRACT

The application hydrogen as energy vector requires the development of new hydrogen storage systems. Challenges in the development of this technology include the design of materials that can achieve the strict requirements of storage capacity and hydrogen release kinetics required for practical applications, and can maintain these properties during the useful life of the product.

Among the different hydrogen storage alternatives studied, hydrides such as magnesium hydride are some of the most promising materials, but these compounds still present thermodynamic (stability) and kinetic (hydrogen release rate) limitations. The production of hydride micro and nanoparticles can contribute to reduce the kinetic limitations, but the preservation of the structure of the nanoparticles during hydrogen cycling, with the associated physical and chemical changes, still is an issue.

The stabilization of hydride nanoparticles in a porous material can improve the kinetics of hydrogen release and contribute to the preservation of the properties of the material by isolation of particles inside the pores of the support material. The objective of this work is to develop a new solid state hydrogen storage material based on hydride nanoparticles stabilized in low-density aerogels.

For this purpose, the production of silica aerogel supports, both as monoliths and as microparticles, has been studied. In order to achieve high hydride loadings preserving the porous structure of the aerogel, magnesium hydride has been loaded into the aerogel by two methods employing supercritical CO₂: impregnation of CO₂-soluble magnesium hydride precursors, and antisolvent precipitation of CO₂-insoluble precursors. The reversible surface functionalization of dry aerogels has also been studied as a tool for modifying the interactions between hydride and support and therefore the deposition of the hydride. The materials obtained have been characterized determining their structural and textural properties, as well as the kinetics of hydrogen release.

INTRODUCTION

In the near future, renewable energies will have to be adopted as the main source of energy due to the depletion of fossil fuels. Establishing a new system based on renewable resources is a challenging task for several reasons, including the fluctuating nature of many renewable energy sources. The direct use of renewable energies in mobile applications is also problematic. A possible solution for some of these problems could be to use hydrogen as an energy vector, that is, as an intermediate between energy production facilities and energy consumption sites that can be stored and transported. In order to make this new paradigm a feasible reality, several technical issues must be solved, including the efficient production and storage of hydrogen, and the conversion to electricity.

Storing hydrogen in small mobile applications can be challenging, since the weight and space required by the hydrogen storage system should be reduced as much as possible. As an example, the US Department of Energy has set targets for onboard hydrogen storage systems for vehicles of 5.5 %wt in 2017 and 7.5 %wt as ultimate target [1]. Several prototypes exist based on the most obvious storage concepts: as a compressed gas or as a condensed gas, but these systems are limited by the physical properties of hydrogen. For these reasons, a considerable effort has been made in order to develop new solid state hydrogen storage systems [2], including hydrides, reaching the development of prototype tanks [3]. Nevertheless, the application of these materials still faces some important limitations, which can be classified into two categories:

- Thermodynamic limitations: most hydrides proposed for hydrogen storage are very stable. High temperatures (200-500°C) are required in order to decompose them.

- Kinetic limitations: Hydrogen uptake and release from hydrides can be very slow.

Simple material processing techniques such as milling are normally used by researchers to solve these limitations, as by particle reduction by milling diffusion lengths are shortened, thus improving kinetics, and a low particle size can contribute to destabilize the hydride and reduce the thermodynamic limitations [4]. However, the preservation of the morphology of particles during hydrogen cycling, with the associated changes in hydride chemical composition, is problematic. Some authors have studied the stabilization of hydrides in mesoporous carbon matrixes in order to preserve their size during hydrogen release and uptake cycles [5].

This work proposes to use silica aerogels, produced by supercritical extraction of the solvent from a gel, as low-weight supports for hydride nanoparticles, with the aim of controlling particle size if the particles are formed inside the pores of the aerogel, since particle growth is restrained by the pore structure of the support. Furthermore, the incorporation of nanoparticles in aerogels can contribute to solve problems of agglomeration and sinterization during hydrogen cycling, because particles are isolated inside the pores of the aerogel. With this objective, results obtained by SAS micronization of hydrides and incorporation in aerogel supports are presented.

MATERIALS AND METHODS

Micronization by SAS process

Supercritical antisolvent precipitation (SAS) was used in order to obtain microparticles of magnesium acetate using methanol as solvent. A custom-design SAS plant, with a precipitator volume of 2.5 L and a maximum CO₂ flowrate of 4 kg/h was employed for this purpose. The

influence of different process parameters: solute concentration, CO₂/solvent flow ratio and temperature was tested.

Formation of aerogel monoliths and microparticles

Silica aerogels were formed by the standard sol-gel method, including:

- 1) Sol-gel reaction, in which a solution of or tetramethoxysilane precursor in methanol is cross-linked by reaction with water.
- 2) Elimination of the solvent from the pores of the gel to produce the nanoporous material by extraction with supercritical carbon dioxide.

The formation of aerogels by supercritical extraction is performed in a high pressure recirculation equipment consisting of an extraction vessel with electrical heating, a CO₂ reservoir, a recirculation pump and a CO₂ compression pump. The drying is performed as follows:

- 1) The gels are loaded into the extraction vessel, submerged in solvent to protect them from mechanical tensions.
- 2) The reservoir is filled with CO₂ in supercritical conditions (typically, at 40°C and 100 bar) using the CO₂ compression pump.
- 3) CO₂ is put into contact with the gel, using the recirculation pump to improve phase contact. During this contact, CO₂ extracts the organic solvent, forming the aerogel. The extraction can be completed in about 4 h, and one or several CO₂ replacements may be necessary during the process in order to remove the last traces of solvent from the aerogel.

Aerogels shaped as monoliths and microparticles. In the case of monoliths, the gel was poured in a mould of the desired size and shape before supercritical drying. Aerogel microparticles were produced by dispersing the alcogel in nonpolar hexane solvent.

Aerogels with hydrophobic surface functionalization were produced using trimethylethoxysilane precursors.

Aerogel loading with hydride

Aerogels were loaded with hydrides by supercritical antisolvent precipitation of the hydride inside the pores of the aerogel, simultaneous to supercritical drying of the aerogel. For this purpose, the hydride was dissolved in the same alcohol employed in the sol-gel reaction. The procedures and equipment used for aerogel drying described in the previous paragraph was used to precipitate the hydrides and dry the aerogels. Aerogels were also loaded with magnesium by impregnation with dibutyl magnesium.

Characterization

Samples were characterized employing the following techniques: laser diffraction for particle size (Autosizer Lo-C, Malvern Instruments), Scanning Electron Microscopy for particle morphology (Jeol JSM 820), X-Ray diffraction (Bruker Discover D8) and FT-IR spectroscopy (Bruker ALPHA) for the structural characterization of the solid, BET measurements for determination of the textural properties of aerogels (Quantasorb Sorption System, Quantachrome Instruments, UK), ICP spectroscopy measurements to determine the metal content in the loaded aerogels, and measurements of the release of hydrogen in a custom designed Sievert's cell for characterization of the hydrogen release properties.

RESULTS

Micronization of magnesium acetate

Figure 1 presents SEM micrographs of unprocessed and SAS processed samples of magnesium acetate. As it can be observed in these figures, a clear reduction of particle size is achieved by SAS processing. The product obtained in SAS experiments was constituted by small spherical particles with a considerable agglomeration. Mean particle size determined by Laser diffraction yielded results ranging from 300 nm to 1.5 μm depending on process conditions.

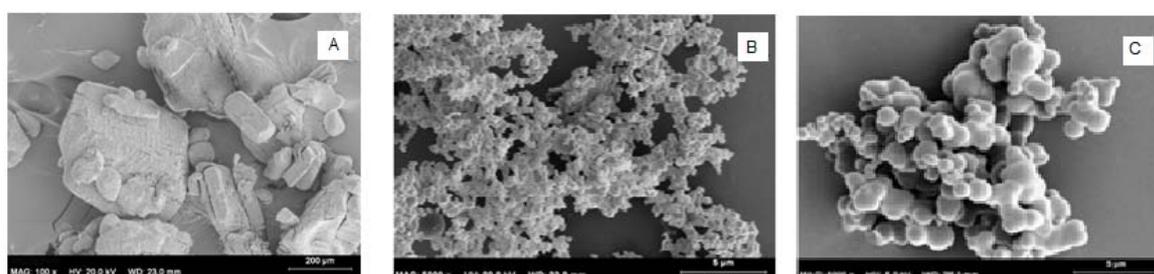


Figure 1: SEM micrographs of: A) Unprocessed material (scale bar 200 μm), B) SAS processed material, 90 bar, 40°C (scale bar 5 μm), C) SAS processed material, 90 bar, 45°C (scale bar 5 μm)

XRD assays showed that while unprocessed magnesium acetate samples were highly crystalline, as indicated by the presence of clear characteristic diffraction peaks at $2\theta = 12, 22$ and 30° , SAS processed materials were amorphous. In general, particle sizes increased when the concentration of magnesium acetate in the initial solution was increased, which is probably connected to the high agglomeration observed in samples, that is promoted when the concentration of compound (and therefore the concentration of particles) is increased. Particle size also increased at higher temperatures, in this case as a consequence of a clear increase on the size of the small particles that constituted the agglomerates, as observed in Figure 1 C.

The organic compound was transformed into a hydride by calcination of the organic part of the molecule and hydrogenation under high temperature and hydrogen pressure (350°C and 22 bar). A successful hydrogenation was confirmed by FT-IR assays, that showed characteristic peaks at wavenumbers of 1450 cm^{-1} , 1550 cm^{-1} and 1600 cm^{-1} . The morphology of particles was partially preserved after hydrogenation of magnesium acetate particles yielded by SAS processing, obtaining particle sizes in the range of 50-100 μm . On the contrary, hydrogenation of unprocessed product yielded compacted particles in the mm - cm size range. Nevertheless, the modification of the morphology associated with the thermal treatment and the variation of chemical composition was obvious, which proves the need for strategies to prevent these modifications such as the incorporation into aerogel supports.

Formation of aerogels

By supercritical drying, as shown in Figure 2 cylindrical silica aerogel monoliths of approximately 3 mm of diameter and 2 cm of height were produced. These monoliths had a surface area of 500 m²/g and a pore volume of 1.25 cm³/g [6]. By supercritical drying of alcogel dispersions in hexane, aerogel particles of 50 μm were produced. These particles had a surface area of 700 m²/g and a pore volume of 0.8 cm³/g.



Figure 2: Aerogel monolith (left) and aerogel microparticle (right)

Functionalization of aerogels

Aerogels with hydrophobic functionalization were synthesized using trimethylethoxysilane precursors during the sol-gel step of the synthesis. The hydrophobic functionalization was demonstrated by FT-IR characterization assays, that showed characteristic peaks at 1300 cm⁻¹ and 800 cm⁻¹ corresponding to CH₃ groups.

Moreover, aerogels were reversibly functionalized by treatment of dry, preformed aerogels with functionalization agents dissolved in CO₂ (trimethylethoxysilane, octyltriethoxysilane or chlorotrimethylsilane). A gradually increasing functionalization was observed as pressure was increased, and therefore the concentration of functionalization agent in CO₂ was increased due to a higher solubility. This functionalization caused a significant reduction of the pore volume, probably by filling or blocking of pores by the functionalization agent [6].

Aerogels loaded with hydrides

By simultaneous alcogel supercritical drying and magnesium acetate supercritical anti solvent precipitation, silica aerogel microparticles were loaded with amounts of up to 65% wt of magnesium acetate, as determined by gravimetric measurements. ICP spectroscopy measurements yielded concentrations of magnesium in the aerogel of up to 7.5 % wt. Samples could be successfully hydrogenated employing the same procedure described for pure magnesium acetate powder, as indicated by the observation of characteristic peaks at 1450 cm⁻¹, 1550 cm⁻¹ and 1600 cm⁻¹ in FT-IR assays. Measurements of hydrogen release kinetics from this materials are in progress.

CONCLUSION

Magnesium acetate as a precursor of magnesium hydride was successfully processed by SAS, reducing particle size to the submicrometer range, but during thermal treatments required for hydrogen cycling the particles showed substantial variations in morphology and increase in size. Incorporation of these particles into the pores of silica aerogels, synthesized as monoliths or microparticles, can contribute to stabilize their morphology. Magnesium loadings in aerogels of up to 7.5 wt% could be achieved.

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