

MICRONIZATION OF MAGNESIUM ACETATE BY SUPERCRITICAL ANTI SOLVENT PROCESS AS PRECURSOR FOR THE PRODUCTION OF MAGNESIUM OXIDE AND MAGNESIUM HYDRIDE

M.Rueda* ,L.M. Sanz-Moral, A.Martín, M.J.Cocero

High Pressure Processes Group.- Department of Chemical Engineering and Environmental Technology
Department, University of Valladolid,c/Prado de la Magdalena s/n, 47011 Valladolid, Spain
e-mail: miriam.rueda.noriega@gmail.com, Tel: +34 983423166

ABSTRACT

Micronization of magnesium acetate tetrahydrate from methanol solutions has been performed by Supercritical Antisolvent (SAS) process at different conditions of operation obtaining spherical particles with an average particle size of less than 1 μ m. Several process parameters: concentration of the solution, temperature and flow of carbon dioxide have been studied analyzing their influence on the properties of particles produced, including its size, morphology and structural properties.

SAS-processed magnesium acetate has been used to obtain two different products: magnesium hydride (MgH₂) and magnesium oxide (MgO).

The utilization of micronized magnesium acetate induces several advantages such as the reduction of diffusion distances enhancing the rate at which hydrogen is distributed to obtain MgH₂. Moreover, hydrogen bond dissociation is also favored enhancing the hydrogen diffusion rate, properties that will improve the kinetic of hydrogen desorption compared to bulk samples. Moreover, magnesium oxide can be used as catalyst in this process in order to speeding-up the hydrogen releasing from the hydride, both products obtained from the same micronized precursor, magnesium acetate.

INTRODUCTION

The development of materials for hydrogen storage is still one of the most important challenges. Magnesium hydride (MgH₂) is one of the most used light metals due to its high content in hydrogen (7.6%wt), light weight and low cost. However, it has some limitations because it requires high desorption temperature and the kinetics of hydriding and dehydriding are slow. Studies have shown that these limitations can be overcome by ball-milling [1] adding catalysts [2] or by chemical modification [3].

Supercritical Antisolvent Solutions, commonly called SAS, is a very promising technique that has been largely used to micronize different compounds: polymers, pharmaceuticals, conductors, explosives, etc. In this work, MgH₂ as hydride and magnesium oxide (MgO) as catalyst has been obtained using micronised magnesium acetate with this technique. The micronization of the precursor is investigated to enhance the kinetics and overcome this limitation [4]. Several process parameters have been studied analyzing their influence on the properties of particles produced. Finally, kinetics of hydrogen release from the resulting hydride have been analyzed employing a volumetric Sievert's apparatus.

MATERIALS AND METHODS

Magnesium acetate tetrahydrate (purity 99.0%) was supplied by Sigma-Aldrich and methanol (99.8% purity) was purchased from Panreac. Carbon dioxide (99.95% purity), which is used as supercritical fluid, was purchased from Carburos Metálicos S.A.

Supercritical antisolvent precipitation (SAS) is the technique used in this work in order to obtain microparticles of magnesium acetate using methanol as solvent. The influence of the temperature (35-45°C), concentration of the solution (10-50mg/mL) and the molar fraction of CO₂ (0.932-0.986) was studied to optimize the micronization process.

The process takes place in a jacketed vessel of 2.5 L of volume which is heated with a water bath. First, preheated carbon dioxide is pumped with a diaphragm pump (Dosapro Milton Roy, Spain) at 2Kg/h until stable conditions are reached. In this moment, the organic solvent is pumped to assure stable conditions in the process. Then, 50mL of the solution is delivered to the precipitator using a chromatographic pump (Gilson mod. 305, maximum flow rate: 25 mL/min, flow rate control with an accuracy of 0.1 mL/min) to be processed. Both solutions are pumped continuously through a coaxial nozzle which is located in the upper zone of the vessel. At the outlet of the vessel, the precipitated particles are collected in a metallic frit.

Another vessel is used to separate the solvent (methanol) and CO₂ after pressure is released in the process which is controlled with a back pressure. Afterwards, CO₂ flow is maintained for 1 hour in order to assure the total elimination of solvent. After the decompression of the system takes place, the particles are collected from the filter and stored under dry conditions.

Once the precursor is micronized using SAS technique, two different products are obtained depending on the treatment of the precursor. On the one hand, magnesium oxide is obtained after calcination at 400°C for several hours in a muffle furnace. On the other hand, processed magnesium acetate is treated with hydrogen at different conditions of pressure P= 20-30 bar and temperature T=350-400°C for several hours in order to remove the organic part and to reduce the metal to obtain the hydride.

Micronized microparticles were characterized using different methods to evaluate the effect of the different conditions of the process. Particle size distribution was measured using a laser diffraction instrument. The morphology of the particles was observed using a Scanning electron microscopy. The phase purity and the crystallinity were examined using an X-ray powder diffractometer (model Bruker Discover D8). Fourier Transform infrared spectroscopy was performed on BRUKER spectrometer (model ALPHA).

The hydrogen release rate from hydrogenated samples was measured employing a volumetric Sieverts' apparatus. For doing so, a certain amount of sample (typically in the range of 0.1g) was weighted and loaded into the apparatus. Then vacuum was applied to the system and it was maintained it at a temperature of 400°C inside a chromatographic oven. The pressure evolution, which is proportional to the amount of released hydrogen, was recorded employing a pressure transducer with an accuracy of 0.001 MPa.

RESULTS

In table 1, a summary of the conditions of the experiments that have been performed and the mean diameter of the particles is reported. In these experiments, the concentration of the initial methanol solution was varied between 10 and 50mg/mL, the temperature in the range of 35-45°C and the ratio between solution and CO₂ reported as CO₂ molar fraction between 0.95 and 0.99; studying their influence on the properties of the product obtained.

Run	T (°C)	C (mg/mL)	xCO ₂	Mean diameter (µm)	Median diameter (µm)
0	unprocessed			200±30	260 ±20
1	40	35.0	0.945	0.69±0.01	1.33±0.01
2	40	31.4	0.945	0.61±0.00	1.16±0.01
3	40	20.1	0.945	0.48±0.00	0.96±0.01
4	40	40.3	0.945	0.74±0.02	1.50±0.04
5	40	50.3	0.945	0.66±0.00	1.48±0.02
6	45	29.9	0.961	0.69±0.02	1.46±0.29
7	35	30.0	0.926	0.52±0.00	1.10±0.06
8	40	30.6	0.958	0.51±0.00	0.98±0.00
9	40	30.1	0.932	0.58±0.01	1.15±0.01
10	40	30.1	0.972	0.57±0.00	1.08±0.00
11	40	30.0	0.986	0.51±0.00	1.08±0.01
12	35	20.0	0.981	0.34±0.00	0.66±0.01
13	35	15.2	0.981	0.29±0.00	0.54±0.00
14	35	10.3	0.981	0.30±0.01	0.60±0.01

Table 1: Experiments performed on AcMg by SAS technique

Regarding the mean diameter, unprocessed MgAc which is a crystalline material, has a mean diameter of 200µm whereas all the micronized particles with SAS technique reduce its size to less than 700nm. Moreover, it is observed in figure 1 that micronized microparticles are spherical. This morphology corresponds to an amorphous crystalline structure, which is also seen in the XRD analysis, compared to a crystalline structure of the unprocessed material also indicated by XRD analysis. On the other hand, figure 2 shows the bimodal particle size distribution (PSD) of the unprocessed MgAc in contrast to unimodal PSD of micronized sample.

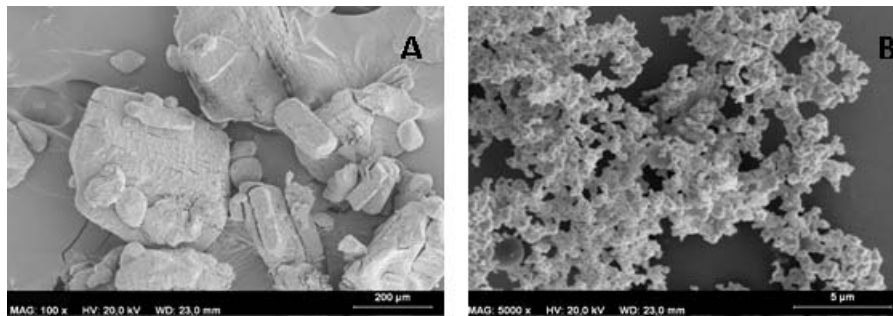


Figure 1: SEM images of Magnesium Acetate, A) unprocessed B) micronized with SAS at 90bar, 40°C and c=31,4mg/mL (run3)

According to the influence of the parameter, the concentration and the temperatures causes a moderately effect on the precipitation of the amorphous microparticles whereas the molar fraction of CO₂ does not have any strong effect on them.

First, increasing the concentration of the solution results in higher particles sizes due a higher agglomeration. In the case of the temperature, increasing temperature results in increasing the solubility of MgAc in methanol which causes the reduction of the supersaturation obtaining higher mean particles sizes at higher temperatures.

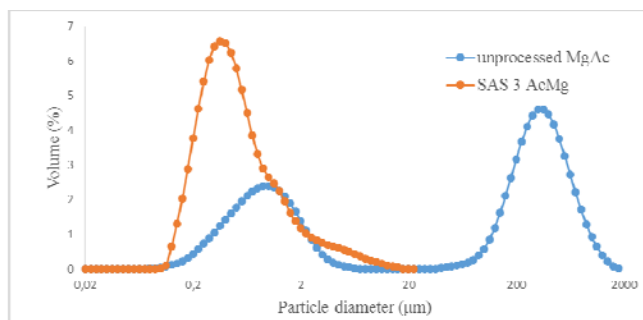


Figure 2: Comparative particle size distribution (PSD) of unprocessed material versus micronised with SAS process.

This compound is used to obtain two different products: magnesium oxide (MgO) and MgH₂. In the case of MgO which is obtained after heating at 400°C, it is seen a remarkable difference between the samples that have been micronized and the unprocessed material. MgO obtained from unprocessed MgAc form a big agglomeration of particles whereas MgO from SAS samples have a grain size between 9 and 12nm. On the other hand, MgH₂ is obtained after treating MgAc with hydrogen at high temperature. FTIR spectra reveals peaks at 1439, 1537 and 1585cm⁻¹ which can be assigned to Mg-nH₂ [5]. Regarding to the kinetic results, it is observed an improvement in the kinetic of dehydrating when the precursor is micronized.

CONCLUSION

Two different products, MgO and MgH₂ are obtained from the same precursor, MgAc, getting different treatments. The precursor is micronized using SAS technique obtaining amorphous microspheres with a significant reduction of the mean particle size, from 200µm with a bimodal distribution of the particles in unprocessed material to less than 1µm and a unimodal PSD. It is also worth to note that this micronization enhance the production of the final material avoiding agglomerations in the thermal treatment. The kinetic of the hydrides and the addition of the catalyst is still under investigation.

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