Materials Research Bulletin 48 (2013) 2817–2823

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Shape controlled synthesis of nanostructured magnesium oxide particles in supercritical carbon dioxide with ethanol cosolvent

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ARTICLE INFO

Article history:
Received 23 November 2012
Received in revised form 18 March 2013
Accepted 2 April 2013
Available online 17 April 2013

Keywords:
Nanoporous
Magnesium carbonate
Magnesium oxide
Supercritical fluids
Carbon dioxide capture and storage
Catalyst support

ABSTRACT

Magnesium compound nanoarchitectures with controlled shape were prepared through carbonation reaction of magnesium hydroxide and carbon dioxide in supercritical carbon dioxide–ethanol mixtures and their formation mechanism were discussed. The leaf-like brucite and the floral-like hydromagnesite nanosheets with a monoclinic structure were formed at the reaction temperature of less than 80 °C and 100 °C, respectively. The floral architecture started to transform the nanosheets with stacked arrangements at the elevated temperature above 130 °C, and compeletely transformed to cube-like magnesite with a trigonal crystal structure at 150 °C in progress of the carbonation reaction of hydromagnesite and carbon dioxide in a supercritical CO_2 with ethanol cosolvent. The morphologies of the product architectures were artificially controlled by the phase transition driven morphological changes. With further increasing temperature to 600 °C, the micro–meso porous magnesium oxide architectures with high surface area were finally formed by decarbonation of the magnesite cubes.

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1. Introduction

Nano-architechtured magnesium compounds have been widely applied in diversified fields as catalyst carriers [1–4], mineral reactants for mineral sequestration [5–7] or carbon dioxide capture and storage [8], an effective antibacterial and anti-odour agent for pharmaceuticals [9], transparent materials [10,11], a remediation agent of toxic waste [12], a deacidification agent for paper conservation [13], and advanced biomaterials [14,15]. Hence, it is very necessary for an elaborate synthesis and tailoring of nanostructures for achieving novel properties that give nanomaterials their exciting utility.

The reactivity of the solid substances is highly influenced by their chemical and thermal prehistory. It is, therefore, no wonder that the fabrications of nano-architechtured materials with controllable size and shape have increasingly attracted much attention [15–21]. However, the production of nanostructures with a reliable and reproducible geometry is difficult to achieve because of the high aggregation propensity of fractal clusters. Recently, much research has been focused on the fabrication of controlled MgO nanostructures by employing different source materials or catalysts [22–24]. Inspite of these trials, the development of a more facile method for achieving MgO nanostructures with controlled shapes and morphologies has been still stimulated by the growing demand for novel materials for potential application in nanocatalysis and nanoelectronics. The synthesis of nanomaterials assisted by supercritical fluids (SCFs) [25–28] has demonstrated great promise, which gives an advantage for growth of particles in a controlled fashion to attain the desired morphology. The properties that make SCFs particularly attractive are gas-like diffusivities, the continuously tunable solvent power/selectivity and the possibility of complete elimination at the end of the process, enabling to rational synthesis of high-quality nanoparticles and their diversified applications.

In this paper, shape controlled synthesis of nanostructured magnesium inorganic products via the carbonation reaction of soluble precursors in a supercritical carbon dioxide fluid with ethanol cosolvent was investigated. Furthermore, magnesium oxide nanoarchitectures with a cube- or a leaf-like feature were prepared through the sequential thermal combustion. In addition, the formation mechanism of the nanoarchitechured magnesium compounds with various shape and size was proposed in detail.

2. Experiment details

Fig. 1 shows schematic representation of the apparatus for nanoparticles synthesis under a SCF condition. The apparatus was designed to carry out fabrication experiment of magnesium oxide nanostructures in the temperature range up to 200 °C and pressure up to 30 MPa. The pressure and temperature in the 316 stainless steel vessel with 300 cm^3 of internal volume were measured with pressure transducers with 0.1% accuracy and with thermocouples

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http://dx.doi.org/10.1016/j.materresbull.2013.04.019

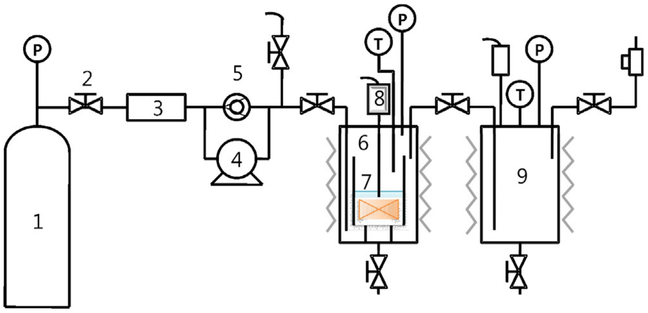

Fig. 1. Schematic representation of the apparatus to synthesize for the nanomaterials using SCF technology: (1) CO_2 reservoir; (2) valve; (3) filter; (4) high pressure pump; (5) back-pressure regulator; (6) experiment chamber; (7) reaction chamber; (8) stirrer; (9) separation chamber.

(±0.1 K). In the middle part of the cell, a transparent window was placed to allow the visual observation of the fabrication process. A duplex high-pressure pump (max. flow rate of 24 ml/min) was used to feed CO_2 continuously from a liquid CO_2 cylinder, via a pre-heater, into the reactor in which the metal precursor solution is filled on glass container.

Fig. 2 shows experimental procedure to synthesize for magnesium oxide nanoarchitectures with various shapes and morphologies using SCFs technology. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 98%, Junsei) was used as a starting material for preparing magnesium oxide precursors. 0.25 mol/l magnesium nitrate hexahydrate was dissolved in ethanol. An ammonia solution (28% NH_3 in water, Junsei) was added dropwise to the mixture slurry while stirring for 30 min, and the pH was adjusted to a value of 9.7. The precipitated slurry was centrifuged and washed three times with ethanol. A volume of 36 ml precipitated slurry was charged with stirring in the viewable reaction vessel of 300 ml, and then introduced CO_2 with a flow rate of 20 ml/min at the temperature of 35 °C to expand the solution until the pressure was reached to 7 MPa, and then the reaction vessel is heated from 80 °C to 200 °C with a heating rate of 3 °C/min and maintained at a desired temperature for 30 min. During the carbonation reaction, the magnesium compounds slurry was converted into magnesium compounds including carbonateous materials in the supercritical carbon dioxide fluid mixtures. The vapour of the organic solvent was mixed with the supercritical CO_2 fluid and removed when the vessel was vented and trapped at the outlet of the installation.

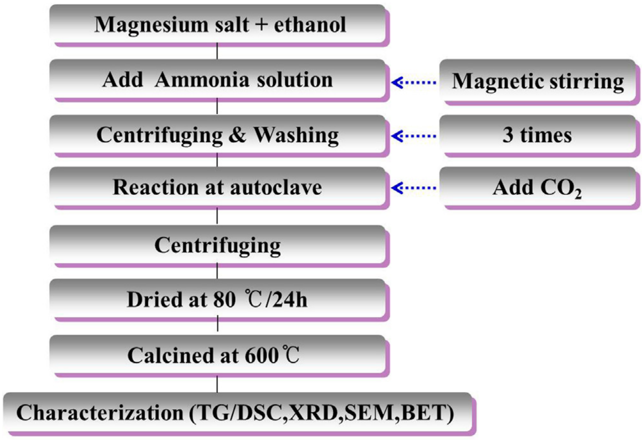

Fig. 2. Experimental procedure to synthesize for magnesium compound nanoarchitectures with various shapes and morphologies using SCFs technology.

When atmospheric pressure was reached the installation was cooled to room temperature. The as-prepared products were dried at 80 °C for 24 h and then calcined at 600 °C for 30 min.

The morphologies, microstructures, and sizes were characterized with a FESEM (Hitachi, S-4100). The crystalline-phase composition was characterized using an X-ray diffractometer (XRD, Cu Kα radiation, Philips X'pert). The magnesium oxide precursor particles were studied via continuous thermal decomposition by thermal gravity, and via differential scanning calorimetry (TG/DSC, Netzsch, STA 409 PC), at a heating rate of 5 °C/min in air. The meso–macro pore structures were investigated using a computer-controlled automated porosimeter (Quantachrome Quadrasorb SI, USA). The specific surface area was determined using a gas sorption analyzer based on the BET (Brunauer–Emmett–Teller) method, and the total pore volume was obtained by converting the nitrogen adsorption amount at a relative pressure of 0.98 to the liquid nitrogen volume. The micropore volume was deduced using the Dubinin–Astakhov method.

3. Results and discussion

FESEM images of Fig. 3 show morphologies and microstructures of the magnesium compound powders prepared at different reaction temperatures of 80 °C, 100 °C, 130 °C, 140 °C, 150 °C and 200 °C, respectively. As shown in Fig. 3a and b, the magnesium compound powders with a leaf-like nanosheet and a floral-like structure were formed at 80 °C and 100 °C, respectively. At above 130 °C, as shown in Fig. 3c and d, some parts of the compound particles with the floral morphology started to break into small pieces and to form the microparticles with stacked arrangements. At higher temperature more than 150 °C, the stacked aggregates are completely transformed to cube-like microparticles with size of 3–5 μm (Fig. 3e and f). We infer that the morphological transition is closely related to phase changes incurred by the carbonation reaction of magnesium hydroxide and carbon dioxide. With further increasing temperature to 200 °C, a morphological change from an inhomogeneous form to a more uniform cube-like shape was observed in the compound particles. Eventually, by the end of the reaction, the compound particles consisted of cubes with relatively smooth surfaces and sharp edges. The growth of the crystalline particles is found to be a time-dependent process. Fig. 4 shows that their original shapes of the magnesium oxide particles with porous nanostructures are still retained after the thermal decomposition at 600 °C.

Fig. 5 shows the X-ray diffraction patterns of the magnesium compounds powders synthesized at different reaction temperatures and the magnesium oxide powders after being heated at 600 °C, respectively. In Fig. 5a, the XRD pattern of the leaf-like magnesium product synthesized at 80 °C matched the reflection characteristic of the hexagonal (rhombohedral) brucite phase of $Mg(OH)_2$ (JCPDS 7-239) with space group P3m1. At the reaction temperature of 100 °C and 150 °C, the magnesium products were identified as $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ crystalline phase with a monoclinic (pseudo-orthorhombic) structure (JCPDS 25-513) and $MgCO_3$ crystalline phase with a trigonal structure (R3c, JCPDS 3-773), respectively. At 140 °C, it is found that the dominant $MgCO_3$ phase and the minor hydromagnesite is coexisting, indicating the monoclinic to trigonal phase transformation, accompanied by the large volume change of more than 34%, occurred. The phases identified by X-ray examinations of powders synthesized at different reaction temperatures were summarized in Table 1.

During aqueous carbonation [29], gaseous CO_2 is firstly dissolved into solution forming carbonic acid (H_2CO_3) in aqueous solution and then the carbonic acid dissociated into the hydrogen

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