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Preparation and characterization of magnesia-coated silica particles by surface-induced precipitation method using magnesia alcoholate precursor

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ABSTRACT

Monodispersed magnesia-coated silica particles were prepared by surface-induced precipitation method using two different magnesia precursors (magnesium alcoholate and magnesium hydroxide) and then calcined at 700 °C. The influence of the alkoxy group on the thermal decomposition behavior and morphological properties of magnesia coated on the surface of silica particles was investigated. The results showed that the degree of the crystallinity of magnesia coating from the alcoholate was significantly higher than that of the hydroxide. Furthermore, the magnesia-coated silica particles obtained from alcoholate exhibited spherical shape without the formation of hard aggregate in spite of heat treatment in comparison to that obtained from hydroxide. XPS investigation also confirmed that the magnesia coating layer and core silica particle were connected through the Mg–O–Si chemical bonding at the interface.

1. Introduction

Magnesia (MgO) particles are one of the most important ceramic materials for a wide range of applications such as catalysts, optical transmitters, pigment, refractory materials, superconductors and packing materials for chromatography [1–5]. From the point of column packing materials' view, high specific surface, dispersion stability and morphological characteristic of the magnesia particles have been identified as the important parameters for high-performance liquid chromatography (HPLC) [6,7]. For this reason, a number of studies have focused on the morphology, size, structure, and other properties of magnesia particles [8,9].

Magnesia particles have been prepared by different techniques including sol–gel [10], precipitation [11], surface-initiated in situ polymerization [12] and hydrothermal synthesis [13], combustion aerosol synthesis [14], etc. In most cases, an additional calcination step is required to transform the amorphous magnesium salts or magnesium complex precursors into a cubic crystalline form of magnesia. However, magnesia particles obtained by these methods were neither spherical nor uniform and had a wide range of particle size distribution. These characteristics are unfavorable for column packing materials. For these reasons, most work in this area has been limited to silica particles due to its spherical shape, narrow particle size distribution, high mechanical strength, packing density, and controllable size. Therefore, a new method to produce the non-agglomerated and spherical magnesia particles is required.

Recently, the homogeneous precipitation coating method using electrostatic attraction process has been extensively investigated to control the shape and uniformity of particles. In particular, core–shell composites with spherical silica microspheres have been widely investigated to provide novel properties that have not been found in the single metal oxide [15]. Moreover, silica particle as a core material offers many advantages such as high specific surface, dispersion stability, narrow particle size distribution, high mechanical strength and controllable size of the particles [16,17]. However, in the conventional coating process of adding a precipitant as a base to a reaction solution, even a weak base added to the solution induces locally higher pH. This leads to inhomogeneous chemical compositions, which contains both the uncoated particles and nano-sized magnesia particles. Moreover, as-prepared particles usually need high decomposition temperature to obtain well-crystalline magnesia particles. The resultant particles have some disadvantages of hard aggregates and incomplete coating surface for the coated particles.

To overcome these problems, magnesium alcoholate complex is proposed as a new precursor of magnesia coating on the surface of silica particles. As a precursor, they can change the decomposition temperature, morphology, porosity and microcrystallinity of magnesia coating which is obtained after thermal decomposition. Thoms et al. [18] investigated the decomposition mechanism of Mg-alkoxide and showed that magnesia morphology is highly dependent on the size of the alkoxy group. Also, Hong and coworkers [19] systematically studied the effects on the decomposition

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and crystallization behavior of magnesia as a function of the alkoxy group. However, magnesium alcoholates as a precursor has not been reported so far for preparing the coated particles.

The present study was intended to establish a novel synthetic method of preparing monodispersed magnesia-coated silica particles for column packing materials with precise morphologies and chemical composition. To achieve that purpose, magnesium ethanolate solvate complex as a new coating precursor was prepared by alkoxide method, which helps to decrease the colloidal interaction and affects the crystallinity and thermal decomposition temperature of magnesia. The effects of magnesium alcoholate as a precursor on the decomposition/crystallization behavior and morphological property of the coated particles were investigated, compared with conventional precursor obtained from water-based solvent.

2. Experimental

2.1. Synthesis

To investigate the effects of solvent type on precursor characteristic, two kinds of magnesium precursor were prepared via different methods using either alcohol-based solvent or water-based solvent. The higher reactivity of ethanol (as alcohol-based solvent) and water allow direct reaction between magnesium metal and the solvent by heating the suspension under reflux. After preparing precursors, magnesia coating was deposited on the surface of bare silica particles via electrostatic attraction route, and then calcined at 700 °C.

2.1.1. Synthesis of magnesium ethanolate complex (designated as precursor A)

The magnesium alcoholate was prepared via mimic alkoxide method. Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) and potassium hydroxide (KOH) were used as starting materials. Magnesium nitrate hexahydrate (10 g) was dissolved in 20 ml ethanol. The solutions were adjusted to pH 10–11 by adding the potassium hydroxide solution under rapid stirring. After maintaining at 70 °C for 6 h, the precipitated product was separated via centrifugation. Eq. (1) describes the exothermic reaction

$$\mathrm{Mg(NO_3)_2 \cdot 6H_2O + 2(CH_3CH_2OH) + 2KOH}$$
$$\xrightarrow{\text{reflux}} \mathrm{Mg(OCH_3CH_2)_2 + 2KNO_3 + 8H_2O} \qquad (1)$$

2.1.2. Synthesis of magnesium hydroxide complex (designated as precursor B)

The magnesium hydroxide was prepared via precipitation method. Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) and potassium hydroxide (KOH) were used as the starting materials. Magnesium nitrate hexahydrate (10 g) was dissolved in 20 ml distilled water. The solutions were adjusted to pH 10–11 by adding the potassium hydroxide solution under rapid stirring. After maintaining at 70 °C for 6 h, the precipitated product was separated via centrifugation. Eq. (2) describes the exothermic reaction:

$$\mathrm{Mg(NO_3)_2 \cdot 6H_2O + 2(H_2O) + 2KOH}$$
$$\xrightarrow{\text{reflux}} \mathrm{Mg(OH)_2 + 2KNO_3 + 8H_2O} \qquad (2)$$

2.1.3. Synthesis of the magnesia-coated silica particles

The silica particles were synthesized by the modified Stöber method [20]. Fig. 1 shows the SEM micrograph of the bare silica particles with mean diameters of 135 nm and smooth surface. For the synthesis of magnesia-coated silica particles, 4 g of the silica particles was dispersed in 40 ml deionized water and 1 g of the precursor was dispersed in 20 ml of deionized water. Magnesium precursor was added into the dispersed silica solution under continuous stirring. The mixed solution was stirred at 80 °C for 5 h after adjusting the pH to 3.0–12.0 with potassium hydroxide solution. The precipitated particles were washed through several decantation and redispersion cycles by centrifugation. The resultant particles were dried at 60 °C for 24 h and calcined at 700 °C for 90 min.

2.2. Characterization

The morphology of particles was characterized by a field emission scanning electric microscopy (FESEM) at an accelerating voltage of 15 kV and a transmission electron microscopy (TEM) at an accelerating voltage of 120 kV. Thermogravimetric analysis (TGA) was performed in an air flow of 100 ml/min at a heating rate of 10 °C/min from 30 °C to 600 °C. The crystalline phase of synthesized particles was determined by a X-ray diffraction (XRD) analysis using CuKα radiation ($\lambda = 0.154$ nm). The infrared spectra, employing a KBr beam splitter and a DTGS detector were recorded in the range 4000–400 cm^{-1} using 64 scans at a resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were performed with a non-monochromatic AlKα source at a base pressure of 5×10^{-1} mbar. As the sample were insulating, the energy calibration was achieved by setting the binding energy of carbon at 284.6 eV.

3. Results and discussion

The compositional changes associated with the calcination process were investigated with thermal analysis. Fig. 2 presents the TGA curves of two kinds of magnesium precursors. The TGA curve of the magnesium ethanolate complex (precursor A) shows three weight losses (curve (a)). The initial weight loss below the temperature of 150 °C can be attributed to the evaporation of physically absorbed water in the air. The second weight loss observed at 280 °C is related to the decomposition of the alkoxy group and organic groups remaining after precursor synthesis. The third weight loss started at about 360 °C is due to the decomposition of magnesium hydroxide leading to crystallization of magnesia and the removal of organic group in the precursor [21]. Meanwhile, the TGA curve of the magnesium hydroxide complex (precursor B) also shows three weight losses (curve (b)). The first step between 80 °C and 150 °C is attributed to desorption of physically absorbed water. The decomposition of the substance continues in the range 280–350 °C due to the decomposition of the salts and ions produced from

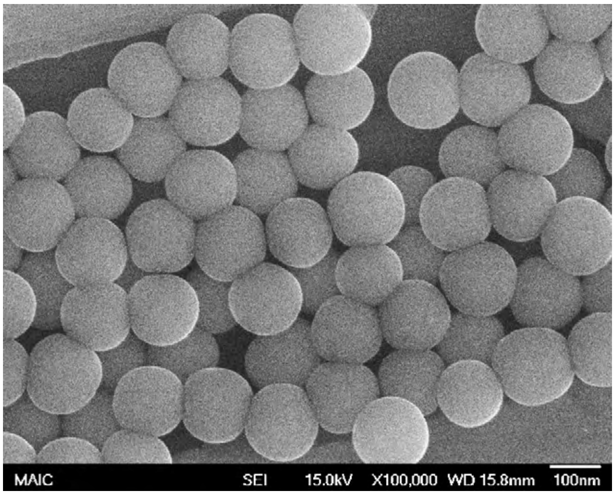

Fig. 1. FESEM micrograph of bare silica particles.