Short communication

Morphology transcription process from CMC micelles to inorganogel and its effect on the properties of alumina particle

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Abstract

In this study, a carboxymethyl cellulose (CMC)-mediated sol–gel process was developed to synthesize the alumina hydroxide whiskers. During the process, inexpensive inorganic salts were used as precursors and supercritical drying method was used to extract the water in hydrogel. The influences of CMC on the gel formation and the particle morphology were investigated. The results show that the formation of CMC–aluminium hydroxide organic–inorganic hybridgels led to a morphology transcription process from CMC micelles to aluminium hydroxide gel, as a result, the precursor with whiskerious morphology was obtained.

Such specific morphology of the precursor delayed phase transformation from transition- to $\gamma$-alumina greatly, and the ability resistant to sintering was highly enhanced. At presence of CMC, the acicular alumina calcined at 1200°C for 4h had surface area of 79.6 m$^2$ g$^{-1}$, much higher than the spherical sample (50 m$^2$ g$^{-1}$) without CMC. Because of being straightforward, inexpensive and versatile, the approach could be potentially used to prepare other materials with controllable morphologies and might be potentially extended to mass-production.

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1. Introduction

Currently, designing of the materials with controllable morphology and microstructure is the interest of researches. Of these, the one-dimensional (1D) nanoscale structures, such as nanowhiskers, nanowires and nanorods etc., are especially interesting due to their excellent physical and chemical properties arising from its nanosized dimension in a certain direction [1–5]. It is well known that the physical properties of a given material are dependent not only on its chemical composition but also on its texture and morphology. For example, Trutrumi et al. [6] have prepared an alumina thin film by using a double-chain ammonium amphiphile as a molecular template, which had a surface area of 100 m$^2$ g$^{-1}$ after calcination at 1300–1500°C; Ishikawa et al. [7] also prepared a thermal stable transitional alumina by fume pyrolysis of boehmite sols. The alumina still possessed a surface area of 50 m$^2$ g$^{-1}$ after calcination at 1200°C for 30h. They ascribed the stability to the suppression of phase transformation from transitional- to $\alpha$-Al$_2$O$_3$ because of a crude structure and fibriform morphology of the particles. In addition, it is known that amphiphilic organic molecules (surfactants, block copolymers, complexing agents, etc.) can self-assemble into various supramolecular structures. The supramolecular structures, as a template, are often utilized to create novel mesophasic inorganic materials [8–10]. Recently, Tillotson et al. [11] have synthesized lanthanide and lanthanide–silicate gels using propylene oxide as a gelation promoter and hydrated lanthanide nitrate salts as precursor.
Itoh et al. [12] have also prepared silicate–aluminate gels using propylene oxide as gelation agent and hydrated aluminum chloride as Al source. In fact, the stable sol could hardly be obtained but precipitating process often takes place during conventional reaction of inorganic salts. Therefore, innovation of a simple and inexpensive method to prepare the stable colloid system is challenged. Basing on the consideration above, we developed a novel CMC-mediated sol–gel method to synthesize the alumina particles. During the process, CMC was used to stabilize the colloid, promote the gel formation and control the particle morphology. The important features of the technology are: (i) It provides with a facile self-assembly route to control the particle morphology. (ii) The technology could potentially be used to prepare other materials with controllable morphologies. The effect of CMC on the morphology, texture, crystal structure and thermal chemical properties of the material was investigated.

2. Experimental

2.1. Chemicals

Distilled water, carboxylmethyl cellulose (CMC, molecular weight, MW = 25,000–35,000), Al(NO$_3$)$_3$ (A. R.), NH$_4$OH solution (25 wt.%, A. R.), absolute alcohol (A. R.). All the chemicals were purchased from Shengyang Chemical Co. in China.

2.2. Preparation of the samples

The Al$_2$O$_3$ samples were typically prepared as follows: (1) Two grams of CMC was added in a 500 ml 0.2 mol L$^{-1}$ Al(NO$_3$)$_3$ solution and refluxed at 80$^\circ$C for 0.5 h to dissolve, then cooled to room temperature. Subsequently, a 1.0 mol L$^{-1}$ NH$_4$OH solution was added into it under stirring with a high-speed emulsifier, while maintaining pH = 9. After aged for 24 h, the hydrogel was filtered and then washed with distilled water and ethanol in sequence. The washed cake was put into an autoclave and dried under supercritical ethanol condition (260$^\circ$C, 8.0 MPa). The details of the supercritical drying method were illustrated elsewhere [13]. Finally, the dried aerogel was calcined in air at 1200$^\circ$C for 4 h. The precursor and the calcined alumina samples were designated as Aerogel$\mathrm{CMC}$ and Al$_\mathrm{CMC}$, respectively. (2) The aluminum hydroxide hydrogel was also prepared from Al(NO$_3$)$_3$ and NH$_4$OH with the same procedure as in (1) but without addition of CMC. After aged and washed, the hydrogel was divided into two parts and dried by the supercritical drying (SCD) and conventional drying (CD) methods, respectively, which were designed as Aerogel$\mathrm{SCD}$ and Xerogel$\mathrm{CD}$, respectively. Then they were calcined under the same condition as in (1), designated as Al$_\mathrm{SCD}$ and Al$_\mathrm{CD}$, respectively.

2.3. Characterization

N$_2$-adsorption experiment was carried out on a Micromeritics ASAP 2010. The particle morphology was characterized by transmission electron microscopy (TEM) on a JEOL 200CX apparatus. The crystal structure analysis of the samples was performed on a Rigaku DMAX-rB X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda = 0.1542$ nm). Elemental analysis was performed on a PHILIPS Magix XRF analyzer. TGA–DTA was carried out with Pyris 1 TGA thermogravimeter and DTA-7 (U. S. Perkin-Elmer Co.)

3. Results and discussion

3.1. The effect of CMC on the properties of the material

Fig. 1 presents TEM images of the precursor samples under different preparation conditions. Without CMC, the precursor sample dried by CD is the large spherical particles with wide size distribution (50–100 nm in size) (Fig. 1a), and the precursor sample by SCD is the uniformed spherical particles with 20–50 nm in size (Fig. 1b). The difference could
be related to the different drying method. It is well known that the interface of gas–liquid disappeared in the SCD process; as a result, collapse of the gel structure was avoided due to the removal of surface tension of water. More interestingly, the precursor sample synthesized in presence of CMC, is nanowhiskers with 1–5 nm in diameter and 50–100 nm in length (Fig. 1c). It could be seen that the presence of CMC molecules has a significant influence on the particle morphology.

Fig. 2 presents TEM images of the alumina particles after calcination at 1200 °C for 4 h. The size of the AlCD sample is distributed in the range of 100–200 nm (Fig. 2a), much larger than that (20–50 nm) of the AlSCD sample (Fig. 2b). This is related to the drying method. At presence of CMC, the acicular particles are about 10–20 nm in diameter and 50–100 nm in length (with an aspect ratio of 3) (Fig. 2c), very different from the nubbly particles of AlSCD and AlCD. Comparing Fig. 1 with Fig. 2, the calcined particles maintained the morphologies of their precursors to some extent, because of a kind of shape memory effect. The acicular particles probably formed by aggregation of much thinner fibrils. Clavier et al. also observed the similar result [14].

Table 1 lists the texture properties of the precursor samples and the calcined samples. After calcination at 1200 °C, the AlSCD sample has higher surface area than AlCD, which may be related to the drying method. The AlCMC sample has surface area of 79.6 m² g⁻¹, pore volume (0.62 ml g⁻¹) and average pore diameter (30.5 nm), much higher than those of the AlCD and AlCD samples. Large pore could refrain ion migration between the particles, so phase transformation and sintering at high-temperature calcination subsequently may be delayed, because only through ion rearrangement can phase transformation occur. Poco et al. [15] reported that
the alumina aerogels do not sinter until above 950 °C. Also evidenced by TGA–DTA and XRD results (Figs. 3–5), the sintering rate of the acicular particles is decreased and their phase transformation to α-alumina is delayed. The different texture properties of the Al SCD and Al CMC samples may be related to their different morphologies. Compared with the spherical particles, one-dimensional materials possess high ability resistant to sintering. Horiuchi et al. [16] have reported that the particle morphology has an important influence on the phase transformation of the material. The contacting chance of the acicular particles is decreased greatly compared with that of the spherical particles [18].

Figs. 4 and 5 show the XRD patterns of the precursor and the calcined samples, respectively. Both of the aerogel samples belong to α-AlOOH structure; the xerogel sample exhibits α-Al(OH)₃ structure. After calcination, all calcined samples contain α-Al₂O₃ and θ-Al₂O₃, but the intensities of the diffraction peaks are different. For the AlC sample, the diffraction peaks of θ-Al₂O₃ are strongest, while the peaks of α-Al₂O₃ are very weak. However, the diffraction peaks of α-Al₂O₃ in AlS and AlCD samples are much stronger than that of θ-Al₂O₃. It could be observed that the phase transformation to α-Al₂O₃ is restrained greatly for the AlCMC sample, also revealed by the DTA–TGA results in Fig. 3. The retardation of phase transformation of alumina seems to be related to the crude acicular structure. Generally, at lower temperature, the intracrystalline micropore for transitional alumina are responsible for high surface areas; α-alumina can form commonly above 1150 °C, which leads to a surface area lower than 10 m² [19]. Therefore, Al CMC sample has larger surface areas than that of the other samples.

3.2. The morphology transcription process from CMC micelle to inorganogel

In presence of CMC, no precipitation was found after ageing for 48 h; without addition of CMC, however, the conventional precipitation process took place as soon as NH₄OH was added. It is clear that CMC could effectively enhance the stability of the colloid system. In fact, CMC aqueous solution possesses 1000 times higher apparent viscosity than...
water even at a low concentration (0.5–3.0 wt.%). The high viscosity is one of the reasons for the high stability of the system. Such thickening effect could protect colloid from precipitation [20]. In addition, since CMC is a poly-hydroxyl polymer (in Fig. 6), hydrogen bonds could form intra- and inter-CMC molecules, which would lead to formation of CMC micelles. Even at lower than 1 wt.%, CMC micelles in solution tangle together to form a rigid claviform- or thread-network with well-defined geometry and shape, e.g., fibers, ribbons, platelets or cylinders etc [21]. Formation of CMC network could be another reason for the stability of the system, because the network of CMC could limit the gel particle aggregation (in Fig. 6, right). The network has been used to control the shape and texture of inorganic materials, e.g., silica and titania [22–28]. Comparing Fig. 1c and Fig. 6, we infer CMC micelles could affect the tropism of aluminum gel. Some kinds of force could drive the aluminum species onto CMC fibers. Addition of NH4 OH would trigger the formation of inorganogel. The CMC fibrous structure could be effectively transcribed into the Al (III) gel. Although the type of interaction between the aluminum oligomers and CMC organogel is still not well clear. We believe that interaction between CMC micelles and inorganogel occurring at the supramolecular level, e.g. H-bonding, van der Waals force, dipole-dipole interaction, electrostatic interaction, coordination bond, etc., may be responsible for the formation of the hybregel, which is similar to what has been suggested for silica fibers templated with DDDA [29] or cationic charged gelators [30]. After ageing, the hybregel framework could be further strengthened.

In a word, the probable formation mechanism of the acicular particles is proposed, shown in Fig. 7. After the CMC organogel formed, the aluminum species could be driven onto the CMC through hydrogen bond and/or van der Waals force. When NH4 OH was added, the aluminum species nucleate and condense on the CMC micelles matrix. While the hybregel was forming, the morphology of CMC organogel could also be transcribed into the aluminium hydroxide gel [31]. The framework of the hybregel is further strengthened after ageing and drying. After calcination, the alumina particles retained their precursor morphology because of a kind of shape memory effect.

4. Conclusion

In this study, we developed a new sol–gel route to synthesize the acicular alumina particles using CMC as gelation agent. CMC plays a significant role in formation of the stable colloid system and in control of the particle morphology. In
addition, because of being straightforward, inexpensive and versatile, the approach could be potentially used to prepare other materials with controllable morphologies and might be potentially extended to mass-production.

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References