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Direct synthesis of Mg/Al layered double hydroxide films with different oriented hexagonal platelets via vapor phase transport and hot water treatment

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Layered double hydroxide (LDH) films with different oriented LDH platelets have been obtained by vapor phase transport and hot water treatment with amorphous precursors, respectively. The effect of preparation conditions, such as varying the crystal growth temperature, crystal growth time and nucleation method is discussed. Furthermore, the mechanisms of the formation of LDH film are also proposed.

Keywords: Layered double hydroxide (LDH) film, Vapor phase transport, Hot water treatment

AIMS AND BACKGROUND

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds, are attracted intensive attention because of their potential applications in wide areas, such as catalysts, catalyst supports and nanocomposites [1, 2]. Structurally, LDHs can be characterized as containing brucite-like layers, where some divalent metal cations have been partially substituted by trivalent metal cations to form positively charged sheets. The charge is compensated by exchangeable anions and water molecules in the interlayers [3, 4]. Owing to their structural anisotropy, new techniques have been recently used to prepare crystalline LDH films. If high quality LDH films can be obtained, their unique electronic, optical and magnetic properties will lead to potential applications in optics, membrane and sensors devices [5]. Pinnavaia et al. [6] have reported that transparent LDH films can be formed by the colloidal LDH suspensions provided through hydrolysis of alkoxide-intercalated LDH derivatives. By the sol-gel process and hot water treatment with the amorphous mixed metal oxides, Yamaguchi et al. have prepared LDH films with high transparency [7, 8]. However, most of the obtained LDH films were not well oriented because these methods were hard to control the orientation of the LDH crystals. In addition, these investigations were only focused on the surface morphologies and properties of the obtained films, but not related to the crystal growth process in course of the formation of LDH films. To explore the crystal growth mechanism of LDH platelets or to observe the assembly of nanosized inorganic particles on solid surface, high quality oriented LDH films originated from amorphous precursors directly is favorable. The preparation method developed in this study for fabricating well oriented LDH thin films including a low temperature deposition (a sol-gel transition) followed by hot water treatment (dissolution-reprecipitation) and vapor phase transport (VPT). According to Xu et al. [9, 10], who first proposed to produce crystalline zeolite by vapor phase transport via the introduction of a vapor mixture with an amorphous dry gel, we tried to vary the nucleation conditions by replacing the hot water with water vapor. Amazingly, these two kinds of treatments with amorphous LDH precursors gave rise to LDH films with different oriented hexagonal platelets.

EXPERIMENTAL PART

Preparation of amorphous precursors

The synthesis of colloidal Mg_2Al-LDH was carried out by a non-steady coprecipitation method [11]. As contrast, we replaced the room temperature deionized water by ice water (3-5 ºC). The pH of an aqueous solution of mixed magnesium and aluminium chlorides (total metal concentration 0.5 M, Mg/Al molar ratio 2:1) was raised to 9.5 by adding diluted aqueous ammonia (1:4 (v/v)) under vigorous stirring. The obtained precipitate was aged in ice bath for 45 min. After filtration, the filter cake was washed thoroughly with ice water to pH about 7.5, and then collected, diluted to 2 wt% and dripped on glass and mica substrates for XRD and SEM measurements, respectively. The coated substrates were dried at the same temperature as the precipitates prepared. After that, one part of the coated substrates were immersed in hot water at 65

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ºC and 80 ºC, respectively, and the others were placed on the supporter of the autoclave whose bottom was filled with deionized water. The autoclave was closed in an oven at 80 ºC, 90 ºC and 110 ºC, respectively. The water vapor forms during heating. After an enough crystallization time of 24h, the substrates were taken out of the reactor and dried at room temperature.

Characterization

Powder X-ray diffraction patterns (XRD) were collected using a Ringku D/MAX-rA X-ray diffractometer with Cu Kα radiation (λ= 1.54184 Å). The surface morphologies of the Mg_2Al-LDH film were characterized by a JSM-6700F field emission scanning electron microscope (FE-SEM) under the following conditions: accelerating voltages (V_{acc}) of 0.5 kV, and emission current of 10×10^{-6} A, a probe current of 7×10^{-12} A and the samples were all treated by performing conductive over-coating of Pt.

RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of Mg_2Al-LDH film formed at different preparation conditions on the glass substrates. The characteristic peaks of crystalline LDH cannot be found in the XRD pattern (Figure 1a), which indicates the amorphous nature of the freshly prepared samples from coprecipitation with ice water. However, two weak peaks are observed in the freshly prepared samples with room temperature water (Figure 1b), most likely because a slow crystal growth occurs under room temperature in time scale (45 min). These results indicate that amorphous nanoparticles are formed instead of crystalline LDH platelets in the coprecipitation and aging processes, especially when the crystal growth temperature is reduced to about zero. This is important for the investigation of the crystal growth mechanisms from an amorphous precursor. After hot water and VPT treatment (Figure 1c-1g), all the samples have three sharp diffraction peaks corresponding to the diffraction planes of (003), (006) and (009) respectively, typical of hydrotalcite-like compounds. The basal spacing is 0.785 nm, which agrees well with the published value for Mg_2Al-Cl-LDH [12]. The absence of (01l) reflections indicates that the samples have high stacking fault density [12], which was not affected by the hot water and VPT treatment. It can be also seen that the intensity of the peak is enhanced while the full width at half maximum is decreased with the increasing of the crystal growth temperature, indicating the crystallinity of LDH platelets is improved.

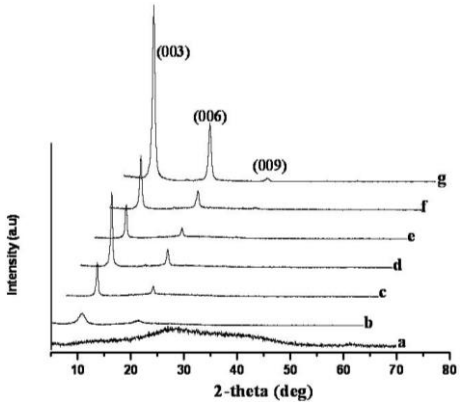

Fig. 1. XRD patterns of Mg_2Al-LDH film formed on glass substrates of freshly prepared LDH with (a)ice water and (b)room temperature water; the same samples as (a) were hot water treatment at: (c) 65 ºC, (d) 80 ºC for 24h and VPT treatment at: (e) 80 ºC; (f) 90 ºC; (g) 110 ºC for 24h, respectively.

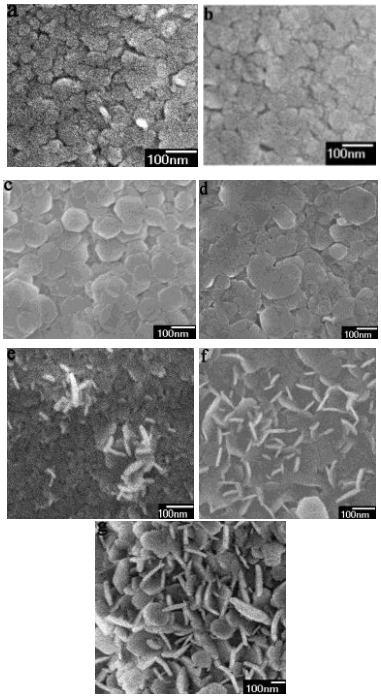

Fig. 2. SEM micrographs of the surface of Mg_2Al-LDH film formed on mica substrates formed of freshly prepared LDH with ice water (a) and room temperature water (b); the same samples as (a) were hot water treatment at: (c) 65 ºC, (d) 80 ºC for 24h and VPT treatment at: (e) 80 ºC; (f) 90 ºC; (g) 110 ºC for 24h, respectively.

The SEM images of LDH films obtained under different crystal growth temperature and time are shown in figure 2, which also confirmed the crystal growth processes of amorphous Mg_2Al-LDH nanoparticles formed after hot water and VPT treatment. The surface morphologies of LDH films formed by the freshly prepared Mg_2Al-LDH precipitates with ice water (Figure 2a) show that they are amorphous aggregates of many ultrafine

nanoparticles. When the coprecipitation and aging processes were carried out under room temperature (Figure 2b), the nanoparticles become larger and much closer to hexagonal in shape, suggesting the slow nucleation and growth of LDH nanoparticles under room temperature. Obviously, for the investigation of the crystal growth process of LDH films, hot water and VPT treatment with the amorphous film (a) is favorable and useful. After crystallization directly in situ on the substrates by immersing the coated substrates in hot water at 65 ºC and 80 ºC for 24h, as shown in Figure 2c and 2d, regular hexagonal platelets and well oriented films were formed. As the crystallization temperature increases, the obtained hexagonal LDH platelets become larger with an arrangement of ab-faces parallel to the substrates.

Surprisingly, when the coated substrates were treated with water vapor at 80 ºC for 24h, hexagonal platelets were also formed. But the orientation of partial LDH platelets becomes ab-faces vertical to the substrates, as characterized by the "bright areas" in Figure 2e. Furthermore, when the temperature of the water vapor is increased to 90 ºC and 110 ºC (Figure 2f and 2g), more and more hexagonal platelets on the surfaces of the obtained Mg_2Al-LDH film are vertical to the substrates and form obvious flowerlike structures. This is consistent with the XRD patterns of the obtained LDH films. Such an orientation with ab-faces vertical and the c-axis parallel to the substrates were observed in Ni-Al LDH films, but in their studies the substrates were pre-treated and the nucleation method was hot water treatment [13,14].

Previously, the formation of crystalline LDH platelets was found to occur in the coprecipitation process, as the fast coprecipitation under room temperature led to a number of uniform nuclei. The following hydrothermal treatment was to improve the crystallinity of the LDH particles and to disperse the initial LDH aggregates into colloidal suspensions [15]. Obviously, crystallization in this way is conflict with our original intention to explore the crystal growth mechanisms of LDH platelets from amorphous precursors. Therefore, we reduce the crystallization temperature to about zero (3-5 ºC), under which we consider the crystal growth to be frozen, and thus gives rise to amorphous LDH precipitates during coprecipitation and aging processes. In the same way, the initial films on the substrates prepared by the deposition and drying processes with a sol-gel transition are also regarded as amorphous.

The process of Mg_2Al-LDH film formation on mica substrates with hot water treatment and vapor phase transport are respectively shown in Figure 3. In the early stage of hot water treatment, the particles firstly experience disaggregation, namely the dissolution of amorphous LDH precursor. After that, the growth of the LDH individual crystallites takes place via Ostwald ripening (the so-called 3-D process including dissolution, deposition and diffusion). Small crystallites dissolve and the Mg and Al species deposit onto the bigger crystallites. Meanwhile, the cations diffuse within the hydroxide layers to reduce the lattice defect and form a better crystallized LDH particle. So we can imagine that a stable monodispersed LDH suspension is formed within the vessel, and thus the particles on the surface of the obtained LDH films are uniform. This indicates that hot water treatment at 65 ºC for 24h is enough to make the amorphous LDH precursors fully crystallize. However, when the hot water treatment temperature is up to 80 ºC, the particles become unhomogeneous because the growth of LDH platelets is increased and reaggregation takes place at higher temperatures. The orientation of hexagonal LDH platelets with ab-faces parallel to the substrates can be attributed to the intrinsic preference of maximum face-to-face contact between the substrates and LDH platelets as well as the adherence of the substrates.

For VPT treatment, the amorphous LDH precursors on the surface of the substrates are actually closed in the water vapor formed during heating, but not brought into contact with the water directly. The water vapor condenses within the dry gel micropores, and thus the upper particles of the amorphous precursors firstly dissolve and crystallization occurs due to a dissolution-reprecipitation process. As a result, the nanoparticles grow outward from the surface of the films with an arrangement vertical to the substrates, which maybe related to the spatial competition between LDH platelets [13]. Although the crystal growth mechanisms under VPT treatment are unclear, these results make us believe that the water vapor has played an important role in controlling the orientations of LDH platelets.

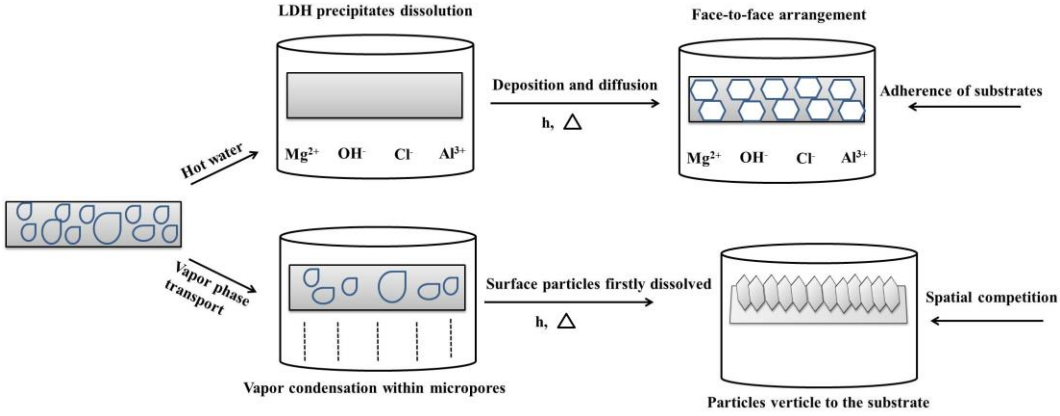

Fig. 3. Schematic of Mg_2Al-LDH film formation on substrates with hot water treatment and vapor phase transport, respectively.

So far as I know, there are rarely reports on the preparation of Mg_2Al-LDH films with VPT treatment from amorphous precursors. However, there are some questions need to be figured out, such as why hot water and VPT treatment result in different arrangement of the hexagonal platelets, how the VPT treatment controls the orientation of the LDH particles? Nevertheless, we provide simple and novel methods to prepare LDH films with different oriented hexagonal platelets. And these questions will be resolved in our further studies.

CONCLUSION

For the applications of LDHs, low costs to manufacturing are very important. Here, we report simple methods to fabricate different oriented Mg_2Al-LDH films via a low-temperature coprecipitation followed by hot water or VPT treatment. The surface morphologies of the produced films are a complex function of many factors, such as crystal growth mechanism, crystallization temperature and crystallization time as well as nucleation and growth environment. For the theoretical studies, the formation of the LDH films can be regarded as the growth of the LDH nanocrystals immobilized on the substrates, which is significant for the investigation of the crystallization process from amorphous precursors. In our further studies, we plan to investigate the optical and magnetic properties of the well oriented LDH films to expand their applications.

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