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Effect of the reaction temperature on nanocrystallites $MgAl_2O_4$ spinel ceramic precursor

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Mg-Al hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$), the precursor of $MgAl_2O_4$ spinel, has been synthesized via a coprecipitation method, using $AlCl_3{\cdot}6H_2O$ and $MgCl_2{\cdot}6H_2O$ as the raw materials, and NaOH and Na_2CO_3 as the precipitators. The effect of the reaction temperature, from 50 °C to 90 °C, on the Mg-Al hydrotalcite nanocrystallites was analyzed. The nanocrystallites were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was confirmed that Mg-Al hydrotalcite nanocrystallites are pure and regularly hexagonal, having a typical hydrotalcite structure. The Mg-Al hydrotalcite crystals grow from about 30 nm to 100 nm with an increase in the reaction temperature from 50 °C to 90 °C, and the crystal form also tends to perfect and regularly hexagonal.

Key words: nano, Mg-A1 hydrotalcite, reaction temperature, coprecipitation, spinel.

Introduction

$MgAl_2O_4$ spinel is a very important ceramic material considering its excellent refractoriness (melting point ≈ 2135 °C), good chemical inertness, high thermal shock resistance and high mechanical strength both at room temperature and elevated temperatures. $MgAl_2O_4$ spinel ceramic has been applied as a refractory, a transparent optical ceramic, as a catalysts and catalyst support, in humidity sensors, for far-infrared window materials, etc [1-4]. The purity of $MgAl_2O_4$ spinel powder is influenced by the synthesis route. In recent years, a novel synthetic method for spinel has been reported. Pioneering work by Liu *et al*. [5, 6], showed that the pure spinel can be obtained by calcination of tailored hydrotalcite-like layered double hydroxides (LDHs) precursors at 900 °C for 2 h.

LDHs are a family of important inorganic materials which have captured considerable attention in recent decades [7]. LDHs can be represented by the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]A_{x/m}^{m-}{\cdot}nH_2O$, in which M^{2+} and M^{3+} are divalent and trivalent metal ions respectively, and A^{m-} is a non-framework charge-compensating intercalated anion [8, 9]. The structure of most of LDHs corresponds to hydrotalcite (HT) with a molecular formula $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$, consisting structurally of brucite-like layers where Mg^{2+}/Al^{3+} partial isomorphous substitution occurs and the resulting net positive charge of the layer is neu tralized by CO_3^{2-}, which also contains water of crystallization.

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Natural hydrotalcite is a rare carbonate mineral, found in small deposits in the Urals and in Norway. Therefore, the preparation of hydrotalcite has been a new hotspot. However, little research has been reported on the effect of reaction temperature on the Mg-Al hydrotalcite so far. In the present study, nano-sized Mg-Al hydrotalcite was synthesized by a coprecipitation method and characterized by XRD, SEM and TEM. The effect of the reaction temperature on the nanocrystallites was investigated.

Experimental

Using $AlCl_3{\cdot}6H_2O$ and $MgCl_2{\cdot}6H_2O$ as the raw materials, and NaOH and Na_2CO_3 as the precipitators, Mg-Al hydrotalcite was synthesized by a coprecipitation method according to the general equation:

$$78Mg^{2+} + 2[Al_{13}(OH)_{32}]^{7+} + 144OH^- + 13CO_3^{2-} + 52H_2O \rightarrow 13Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O \quad (1)$$

A solution containing 0.12 mol of $MgCl_2{\cdot}6H_2O$ and 0.02 mol of Na_2CO_3 in 400 ml of water was added dropwise to an aqueous solution of $AlCl_3{\cdot}6H_2O$ and Na_2CO_3, with a constant molar ratio of Mg/Al of 3. The pH was controlled to around 13. The reaction proceeded in a water bath at various temperatures from 50 °C to 90 °C under vigorous stirring for 6 h to obtain a homogeneous suspension. The suspension was aged and washed with distilled water again and again till the pH was nearly neutral. Then it was filtered and finally dried at 100 °C for 5 h.

The Mg-Al hydrotalcite obtained was characterized by X-ray powder diffraction, using a D/MAX-RA X-ray diffractometer with Cu K_α radiation ($\lambda = 0.154184$ nm) from $2\theta = 10°$ to 74.5°, operated at 40 kV and 100 mA. A FEI

QUANTA200 SEM was used to observe the particle morphology of the samples. The crystal structures were examined using a HITACHI H-7650 TEM.

Results and Discussion

XRD patterns of the samples formed at different reaction temperatures are shown in Fig. 1. All samples crystallized only as a pure hydrotalcite-type phase (JCPDS 22- 0700) and showed symmetrical and sharp peaks, which gives a clear indication that the samples were well crystallized. The peaks corresponding to (003), (006), (009) and (110) planes are characteristic of the clay mineral (hydrotalcite) having layered structure. The (003) and (006) reflections give the basal interlayer spacing $d_{(003)}$. The (110) planes reflect the charge density of laminates [10]. Fig. 1 clearly indicates that the intensity of the corresponding peaks increases with an increase in the reaction temperature, and the crystallization tends to be more ideal.

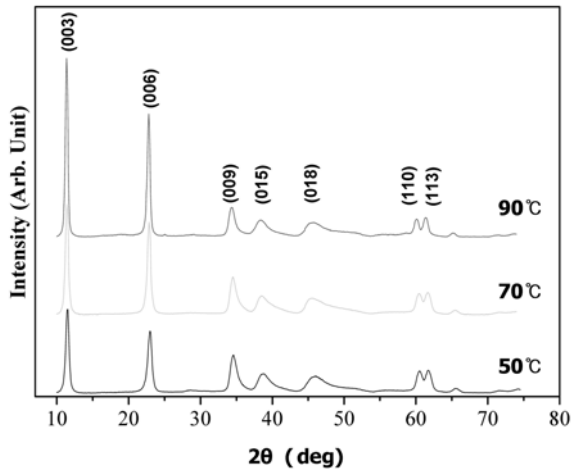

Fig. 1. X-ray diffractograms of the samples formed at different reaction temperatures.

The grain sizes of the samples were calculated by the Scherrer formula:

$$D = \frac{K\lambda}{\beta cos\theta} \quad (2)$$

in which K is a numerical constant with a value of 0.89, λ is the wave-length, β the half-value width and θ the Bragg angle. Evidently, the largest crystals were formed was gained at 90 °C, because the grains gradually grew up with an increase of the reaction temperature in a certain range. Ion diffusion become easier with an increase in the temperature, the larger crystal grains annexing the smaller results in a decrease in the grain boundary and surface energy content. And then the larger the crystallite size, the more energetically stable.

Reaction temperature affects not only the grain size of Mg-Al hydrotalcite, but also the morphology. Fig. 2 shows the morphological features of these samples prepared at 50 °C, 70 °C and 90 °C. From Fig. 2, we can see that the higher the reaction temperature, the bigger are the Mg-A1 hydrotalcite particles, and the lamellar structures which are made up of many smaller particles are more and more obvious. It is deduced that the grain size of Mg-A1 hydrotalcite increases with an increase in the reaction temperature, and the crystal structure tends to stabilize.

The TEM images of hydrotalcite samples formed at different reaction temperatures are shown in Fig. 3. Ethanol

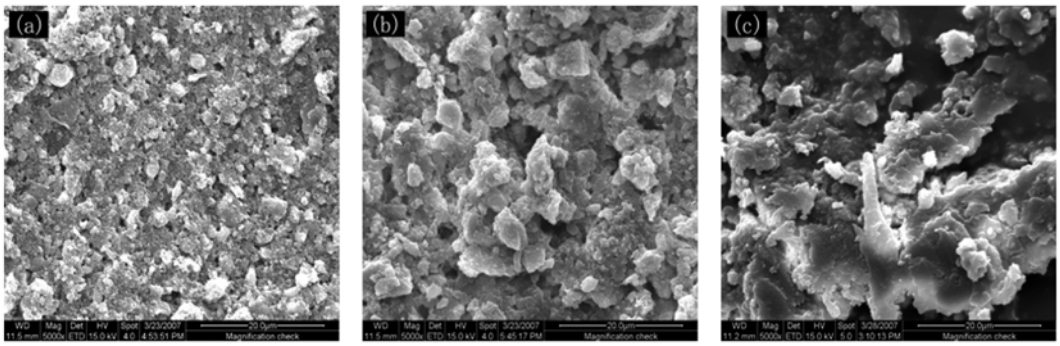

Fig. 2. SEM images of Mg-Al hydrotalcite formed at different reaction temperatures (a)50 °C (b) 70 °C (c) 90 °C.

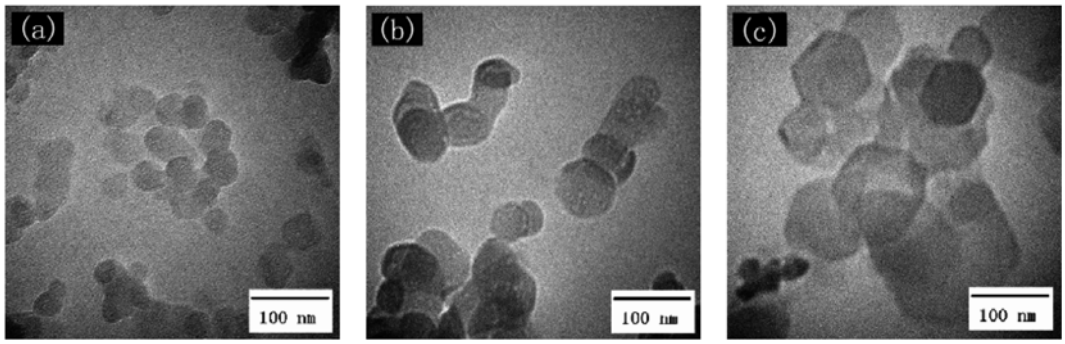

Fig. 3. TEM images of the Mg-Al hydrotalcite formed at different reaction temperatures (a) 50 °C (b) 70 °C (c) 90 °C.

was used as a dispersant, and ultrasonic oscillation was introduced to decrease the aggregation. Apparently, with an increase in the reaction temperature increasing from 50 °C to 90 °C, the grain size changes from about 30 nm to 100 nm, and the crystal form also tends to be more perfect and regularly hexagonal. We can see that well-defined hexagonal sheet crystals are formed at 90 °C, and the crystals are so thin that they are nearly electron transparent.

Conclusions

Mg-Al hydrotalcite nanoparticles were successfully synthesized by a liquid coprecipitation method using $AlCl_3 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ as the raw materials, and NaOH and Na_2CO_3 as the precipitators. The results show that the Mg-Al hydrotalcite crystals grow from about 30 nm to 100 nm with an increase in the reaction temperature from 50 °C to 90 °C, and the crystal form also tends to be perfect and regularly hexagonal. Moreover, well-defined hexagonal sheet crystals of Mg-Al hydrotalcite were obtained when the reaction temperature was 90 °C.

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