

Preparation and surface modification of magnesium hydroxide in a cetyltrimethyl ammonium bromide/isopropanol/cyclohexane/water microemulsion

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A scalable technique for controlled synthesis and surface modification of magnesium hydroxide using the microemulsion method at room temperature was studied. The magnesium hydroxide nucleation and growth were carried out in numerous identical nanoreactors formed by cetyltrimethyl ammonium bromide/isopropanol/cyclohexane/water microemulsion. The crystal structure, morphology, thermostability and surface performance of the product as flame-resistant material were investigated by X-ray diffraction, scanning electron microscopy, thermogravimetry/differential scanning calorimetry, fourier transform infrared spectroscopy and dispersion tests. The results indicated that the product had a flake structure and belonged to a hexagonal system, the highly defined nanoflakes had a uniform diameter, and the diameter size can be well controlled in the range of 40–65 nm by adjusting the ratio of water to surfactant. The thermostability analyses showed a narrowed decomposition temperature range. Furthermore, the surfactant in microemulsion was adsorbed on the particles surface, making the surface of magnesium hydroxide changed from hydrophilic to lipophilic. Therefore the reported magnesium hydroxide material has a better flame resistance and compatibility with polymer materials than conventional magnesium hydroxide.

1. Introduction: The demand for environmentally friendly flame retardant increases continuously with the growing environmental awareness and prohibitive legislation [1]. Magnesium hydroxide, especially the ultrafine magnesium hydroxide, has attracted more and more attention for its good flame retardant characteristic, low economic cost and excellent environmental performance [2, 3]. Some methods have been used to prepare ultrafine magnesium hydroxide, such as the precipitation method [4–6], hydrothermal route [7, 8] and solvothermal reaction [9]. However, magnesium hydroxide synthesised in the above research is in a wide particle size distribution and tends to agglomerate. Besides, the magnesium hydroxide surface shows a hydrophilic characteristic, which results in bad dispersion and is difficult to miscible in polymers. The good dispersibility is the point of magnesium hydroxide used as polymer fillers, so the surface treatment of magnesium hydroxide is necessary during its application process. It has been reported that magnesium hydroxide can be successfully modified by oleic acid, hexylphosphoric acid and vinyltriethoxysilane [10–12], but the synthesis process is complicated and costs too much.

The microemulsion method is well known as one of the nanometre material preparation technologies, which uses ‘water-in-oil’ or ‘oil-in-water’ microemulsion droplet as a ‘nanoreactor’. The nucleation, growth and coalescence processes can be confined to the tiny spherical droplets so as to control the particles size [13]. At the same time, the adsorption effect of surfactant can reduce the surface tension of the particles and prevent the primary particles from the reunion. At present, the microemulsion method has been successfully used to prepare dispersible inorganic nanoparticles, such as ZnO, Li₂O/MgO, ZnMn₂O₄ etc. [14–16]. As to magnesium hydroxide, Ganguly [17] chose ammonium oxalate as a precipitant and used the double microemulsion method to prepare a magnesium hydroxide precursor for further preparing magnesium oxide, the regulation of microemulsion and the quality of magnesium hydroxide were not discussed. Wu [18] prepared 20 nm thickness slice of magnesium hydroxide using the triton X-100/cyclohexane/*n*-hexanol/water microemulsion system, but due to the collision of micelles, the nanoparticles appeared to coalescence and the particle size distribution range was wide. Our study provides an important insight into the morphology control and uniform size distribution of magnesium hydroxide, at the same time, surface

modification is realised in situ to achieve better compatibility with a polymer matrix.

In this work, magnesium chloride hexahydrate was used as the aqueous phase; cyclohexane was used as the oil phase. The ionic surfactant, cetyltrimethyl ammonium bromide (CTAB), and a co-surfactant, isopropanol, were used to form a w/o microemulsion. Sodium hydroxide was chosen as the precipitant to add to the microemulsion above for preparing magnesium hydroxide at room temperature. The morphological structures of the powders were analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The thermal stability and surface performance of magnesium hydroxide affected by CTAB were investigated by thermogravimetry/differential scanning calorimetry (TG/DSC) and Fourier transform infrared (FT-IR) spectroscopy.

2. Experimental: Magnesium chloride hexahydrate, sodium hydroxide, cyclohexane, isopropanol and ethyl alcohol were purchased from Tianjin Guangfu Technology Development Co. Ltd (Tianjin, China). CTAB (99%) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). All chemicals were of analytic grade and used without further purification and/or treatment. Deionised water was used in all experiments.

In a typical experimental process, 2 g CTAB was dissolved in 10 ml cyclohexane and 5 ml magnesium chloride hexahydrate solution (1 mol/l) during stirring, and then 5 ml isopropanol was introduced drop-wise to the mixture and a sub-transparent microemulsion was observed. The microemulsion was then further stirred for 30 min to achieve steady state. Different microemulsions can be obtained by adjusting the ratio of magnesium chloride hexahydrate to CTAB (R). The corresponding synthetic conditions are listed in Table 1.

After the microemulsion was prepared, 10 ml of sodium hydroxide (1 mol/l) was added. After 30 min stirring and 2 h aging sequentially, the white magnesium hydroxide precipitate was obtained. Magnesium hydroxide precipitate was separated by centrifugation at 12,000 rpm, and the resulting precipitate was washed twice with ethanol and deionised water, respectively, followed each time by additional centrifugation. The washed precipitate was dried for 12 h at 80°C for further characterisation.

Table 1 Detailed synthetic conditions of different microemulsions

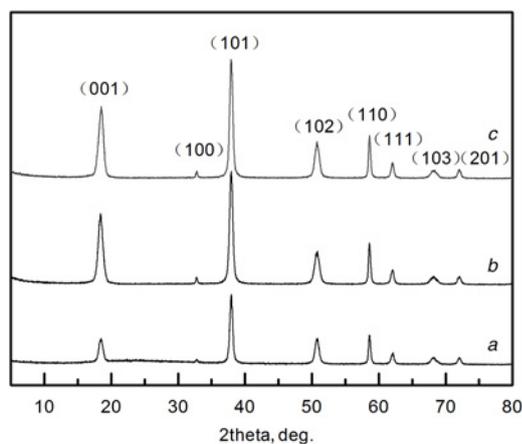
Cyclohexane, ml	MgCl ₂ ·6H ₂ O, ml	CTAB, g	Isopropanol, ml	(R)
20	1	4	5	5
10	5	2	5	50
10	5	1	5	100

The phase structure of the as-prepared products was investigated by XRD on a D/MAX-2500 diffractometer (Rigaku, Japan) operating at 100 mA and 40 kV using monochromated Cu K α radiation ($\lambda = 1.541 \text{ \AA}$). The morphology and size of the as-prepared products were observed by SEM on a Nanosem 430 (FEI, USA) operated at 15 kV. TG/DSC analysis was carried out on a STA449F3 thermoanalyser (Netzsch, German), under a N₂ atmosphere, at a heating rate of 10°C/min. The FT-IR spectrum was recorded on a MAGNA-560 spectrometer (Nicolet, USA) with the KBr pellet method in the range of 400–4000 cm⁻¹.

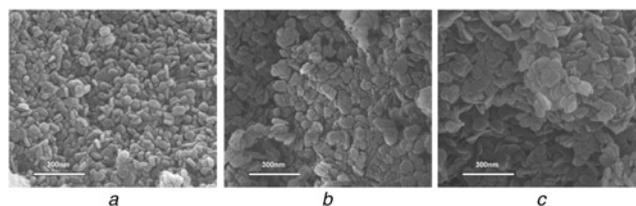
3. Results and discussion: The typical powder XRD patterns of magnesium hydroxide are shown in Fig. 1, the diffraction pattern of the magnesium hydroxide has eight broad peaks at 18.46, 32.78, 37.92, 50.78, 58.62, 62.06, 68.24 and 72.06°, corresponding to (001), (100), (101), (102), (110), (111), (103) and (201) of magnesium hydroxide (JCPDS Card No. 7-239), respectively. The diffraction peaks of magnesium hydroxide are sharp and intense, indicating their highly crystalline nature. No impurity peaks were observed, confirming the high purity of the products. Therefore, the crystal structure of magnesium hydroxide was not affected by microemulsion system.

Comparing XRD patterns of a, b and c, it can be found the diffraction pattern becomes more and more sharp with the increase of the molar ratio of water to CTAB (R), indicating that the sample's crystallinity increases. It can be attributed to the different microemulsion droplet sizes. The microemulsion droplet volume has a positive correlation to the molar ratio of water to CTAB, which is benefit for the magnesium ions growth on the surface of magnesium hydroxide particles and providing sufficient space for lattice arrangement.

Fig. 2 shows the SEM images of the magnesium hydroxide with different R, in which the magnesium hydroxide has a uniform flake structure and the particles are well dispersed in nanoscale. The size of magnesium hydroxide particles is mainly influenced by the

**Fig. 1** XRD patterns of magnesium hydroxide with different molar ratios of water to CTAB (R)

a R=5
b R=50
c R=100

**Fig. 2** SEM images of magnesium hydroxide with different molar ratios of water to CTAB (R)

a R=5
b R=50
c R=100

size of the microemulsion droplet. In general, the microemulsion droplet size is nanoscale, so the resulting product is at the nanoscale. In this w/o microemulsion system, the magnesium chloride hexahydrate solution was used as the aqueous phase and segregated by the continuous organic phase. The sodium hydroxide was added into this microemulsion system as a precipitating agent. The OH⁻ passed through the interface membrane and reacted with Mg²⁺ in the aqueous phase to form magnesium hydroxide crystallites. All the stages of nucleation, growth, and crystallisation of nanoparticles were performed in the aqueous phase, the product size was maintained in a certain range, so the particles size distribution was narrowed and uniform.

The molar ratio of water to surfactant (R) is the determining factor in controlling the size of a water droplet in the microemulsion. As shown in Fig. 2, the mean sizes of particles for samples a, b and c are 44.74, 55.59, and 63.23 nm, respectively. This is in accordance with the sequence of water to surfactant ratios in the samples, demonstrating the R is of great significance to the size control of magnesium hydroxide particles. Furthermore, the hydrophobic of magnesium hydroxide was enhanced, due to the surfactant CTAB adsorbed on the surface of magnesium hydroxide, the dispersibility of magnesium hydroxide has been improved by avoiding the reunion of particles. Fig. 3 shows the growth mechanism schematic.

TG and DSC curves were determined to investigate the thermal stability of the magnesium hydroxide sample, as shown in Fig. 4. The TG curve displays the slow weight loss stage in the temperature range from 100 to 320°C corresponding to the release of H₂O and surfactant adsorbed on the surface of the sample. The obvious weight loss stage is ascribed to the decomposed of magnesium hydroxide in the temperature range from 320 to 410°C. Given the observed weight loss rate of about 26.7% in this temperature range, this weight loss is slightly less than the theoretical weight loss of magnesium hydroxide (30.89%) [4]. It can be ascribed to the surfactant adsorbed on the surface of magnesium hydroxide that affects the decomposition of magnesium hydroxide.

The DSC curve of the sample shows two apparent peaks, one curve is gradual and can be observed around 100°C, the other begins at about 320°C, and the maximum heat flow is observed around 387.5°C, which is higher than other methods reported [4, 5, 8]. The high pyrolysis temperature can allow synthetic materials to add magnesium hydroxide to withstand higher-processing temperature. After 410°C, both the curves are relatively flat; the sample decomposes completely and generates the stable and high-temperature resistant magnesium oxide. The release of H₂O plays an active role to dilute the concentration of oxygen and combustible gas during the combustion of synthetic materials.

FT-IR analysis was carried out to verify the change of the magnesium hydroxide surface structure using the microemulsion method. As shown in Fig. 5, the intensities of the FT-IR peaks corresponding to magnesium hydroxides, such as the O–H stretching vibration peak at 3698 cm⁻¹ and the Mg–O stretching vibration peak at 458 cm⁻¹. Significantly, the new stretches at 2926 and 2851 cm⁻¹ can be assigned to asymmetric and symmetric vibration

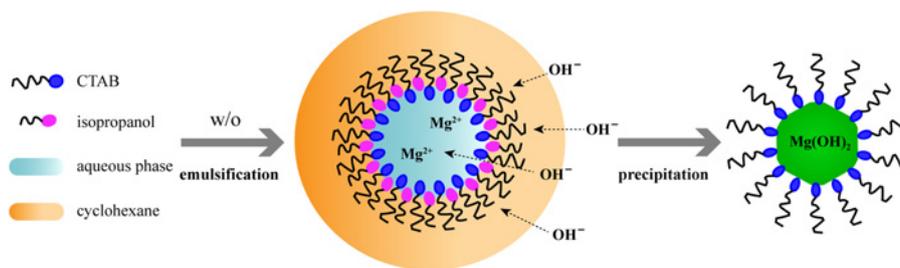


Fig. 3 Schematic illustration of the growth mechanism of magnesium hydroxide in the microemulsion system

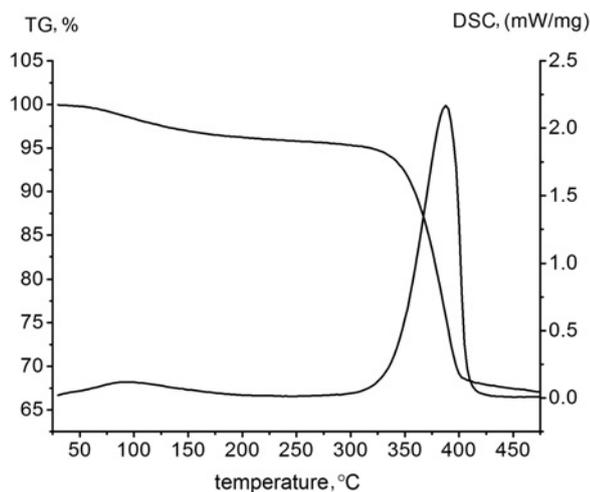


Fig. 4 TG/DSC curves of magnesium hydroxide sample



Fig. 6 Distribution of magnesium hydroxide in the mixed solution of water and toluene

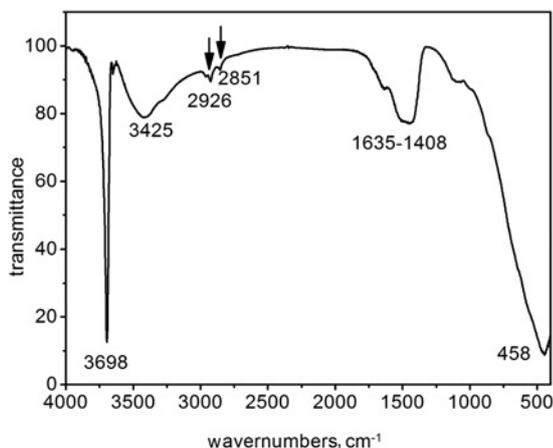


Fig. 5 FT-IR patterns of magnesium hydroxide

of the C–H (–CH₃ and –CH₂–), indicating that the surfactant CTAB still existed on the surface of particles after washed with ethanol and deionised water. In addition, the broad peak at 3425 cm⁻¹ belongs to the stretching vibration of the absorbed water [19], the overlaid peaks in the range of 1408–1635 cm⁻¹ are attributed to the O–H stretching vibration peak in water or the CH₂ scissoring peak in the CTAB [20]. The presence of CTAB is helpful for the high dispersibility of nanoparticles and miscibility with the organic phase when used as a flame retardant.

To further investigate the surface performance of magnesium hydroxide, the experiment of the magnesium hydroxide sample distributed in the mixed solution of water and oil was studied. Fig. 6 shows the magnesium hydroxide powder added into a 1:1

water-toluene system, after enough oscillation, the mixture was then deposited for 24 h. In the end, the toluene phase appears cloudy and forms a homogeneous suspension, but the aqueous phase is clear. It can be interpreted as the CTAB stretching in the dispersing medium and forming a stable hindrance layer between the particles, which enhances the non-polar degree of the magnesium hydroxide surface, and the surface structure changed from hydrophilic to lipophilic, which is more easily dispersed in non-polar solvent toluene. The magnesium hydroxide has a better lipophilic surface performance without additional modification operation using this microemulsion method, which has the advantage in the flame retardant application by adding into the polymers directly.

4. Conclusion: A novel technique is reported for the synthesis of nano-magnesium hydrate of uniform diameter and lipophilic surface in a CTAB/isopropanol/cyclohexane/water microemulsion reactor. The molar ratio of water to CTAB has a significant influence on the particles size, which could adjust the particles in the range of 40–65 nm. The pyrolysis temperature of magnesium hydroxide is higher than the conventional magnesium hydroxide, as shown by TG/DSC analysis, which indicates magnesium hydroxide in this method can be used for a higher-processing temperature of the synthetic materials. Surface performance analysis shows that there is surfactant CTAB from the microemulsion system adsorbed on the surface of magnesium hydroxide. The coating of CTAB enhanced the surface lipophilicity of magnesium hydroxide, making it easier to be miscibility with the organic phase. Therefore this synthesised magnesium hydrate exhibits better flame retardant performance and process ability in polymer material without further modification operation, which may have potential direct application in a flame retardant filler for polymers.

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6 References

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