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温和条件下混合碱辅助水热合成硅酸镁纳米管

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摘要:在混和碱的辅助下,以普通氢氧化镁和二氧化硅粉末为原料在温和条件下高效合成硅酸镁纳米管。采用 XRD,TEM,FTIR,氮气吸附等多种手段对产物进行了表征,并对其合成过程进行了研究。结果表明氢氧化钠和氢氧化钾的共融液能提高反应物间的溶解性,促进反应可以在温和条件下加快进行。250 ℃下合成硅酸镁纳米管,传统水热法至少需要 7 d,混合辅助水热合成只需 36 h。与传统的水热法相比,混和碱辅助的水热法是一种温和且高效的过程。

关键词:纳米管;水热合成;硅酸镁;混合碱;共熔液
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Composite-Hydroxide-Assisted Hydrothermal Synthesis of Magnesium Silicate Nanotube

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Abstract: A mild and highly efficient hydrothermal synthesis method for uniform magnesium silicate nanotubes was developed from normal $Mg(OH)_2$ and SiO_2 powders with the assistance of potassium hydroxide and sodium hydroxide. The samples were characterized by XRD, TEM, IR, and nitrogen adsorption-desorption. The synthetic process was studied by XRD, TEM, etc. The results indicate that the eutectic solution of potassium hydroxide and sodium hydroxide offers higher dissolvability for the reactants and benefits the reaction between the reactants. This composite-hydroxide-assisted approach is a mild and highly efficient procedure for the synthesis of high quality magnesium silicate nanotubes at 250 ℃ in a short duration of 36 hours, while it needs over 7 days at 250 ℃ for traditional hydrothermal method.

Key words: nanotube; hydrothermal synthesis; magnesium silicate; composite-hydroxide; eutectic solution

Since the discovery of carbon nanotubes in 1991 by Iijima[1], one-dimensional(1D) nanostructures with hollow interiors have attracted much attention due to their marked shape-specific and quantum size effects[2-4]. The unique physical and chemical properties of the tubular-structured materials have been well documented and proposed for varied applications[5-9]. By now, apart from widespread carbon-based nanotubes, a great many other inorganic nanotubes have been intensively explored[10-15]. Among them, magnesium silicate, especially $Mg_3Si_2O_5(OH)_4$ nanotubes, have attracted special interests because of their structural similarity to the natural mineral chrysotile and their important application in the development of polymer-inorganic nanocomposites[16-18].

In the natural world, serpentine with empirical

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formula $Mg_3Si_2O_5(OH)_4$, is one type of magnesium silicate minerals with layered structure, in which a sheet of Si-O tetrahedrons joins with a sheet of Mg-O octahedrons through the shared apical O atoms to form a layer[19]. Chrysotile, as one kind of serpentine fibrous minerals, is caused by the cylindrical roll of the layers, which forms tube-like morphologies. This incombustible, chemical-resistant, fibrous mineral can be used in flame retardance, electric insulance, hydrogen storage, waste water treatment, catalysis and so on[20-23]. With the development of varied applications, synthetic nano-sized chrysotiles, i.e. $Mg_3Si_2O_5(OH)_4$ nanotubes, have attracted increasing attention. Since one of the first systematic studies on the synthetic serpentine under hydrothermal conditions was reported in the 1950s by Roy and co-workers[24], many efforts have been devoted to synthesize magnesium silicate nanotubes mainly using solvothermal method, hard template method and hydrothermal method[25-28]. Among them, the hydrothermal synthesis of $Mg_3Si_2O_5(OH)_4$ nanotubes (chrysotiles) from normal SiO_2 and $MgO/Mg(OH)_2$ powders have attracted most attention due to the low-cost and easy large-scale preparation[25-27]. Because of the low reactivity of the starting materials (normally, the powders possess size of submicron to hundred microns), however, the hydrothermal synthesis needs to be implemented at high temperature and pressure, i.e. 300~400 ℃ and 30~100 MPa. Therefore, seeking a simple approach for low-cost, lower-temperature, lower-pressure, controlled synthesis of $Mg_3Si_2O_5(OH)_4$ nanotubes from normal SiO_2 and $MgO/Mg(OH)_2$ powders is highly desired. Recently, Jancar and Suvorov[29] reported the hydrothermal synthesis of chrysotile $Mg_3[Si_2O_5](OH)_4$ nanotubes from amorphous SiO_2 (hydrolysed from Tetra-ethyl-ortho-silicate) and control-prepared nanocrystalline $Mg(OH)_2$ at 200 ℃ for 5 days. Their study revealed that the conversion of $Mg(OH)_2$ took a long time even for ~20 nm nanocrystalline $Mg(OH)_2$ with higher reactivity. To date, the synthesis of $Mg_3Si_2O_5(OH)_4$ nanotubes from normal SiO_2 and $MgO/Mg(OH)_2$ powders under mild condition has been still a challenge.

Herein, we report a novel and facile composite-hydroxide-assisted hydrothermal process to synthesize $Mg_3Si_2O_5(OH)_4$ nanotubes from normal $Mg(OH)_2$ and SiO_2 powders at 250 ℃ in a short duration. The current method is proved more efficient for the precursor formation, and then benefits the formation of the $Mg_3Si_2O_5(OH)_4$ nanotubes.

1 Experimental

1.1 Characterization

X-ray diffraction (XRD) analysis was performed on a Philips X′Pro X-ray diffractometer with Cu $K\alpha$ irradiation (λ=0.154 18 nm) at 40 kV and 40 mA. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were conducted with JEM-100S and JEM-2010 electron microscopes, using an accelerating voltage of 80 kV and 200 kV, respectively. Nitrogen sorption isotherms were collected at 77 K using Micromeritics ASAP2020 equipment. Fourier transform infrared (FTIR) spectra was recorded on a Bruker Vertex 70 spectrophotometer with KBr pellets, at 64 scans with a resolution of 4 cm^{-1}.

1.2 Preparation

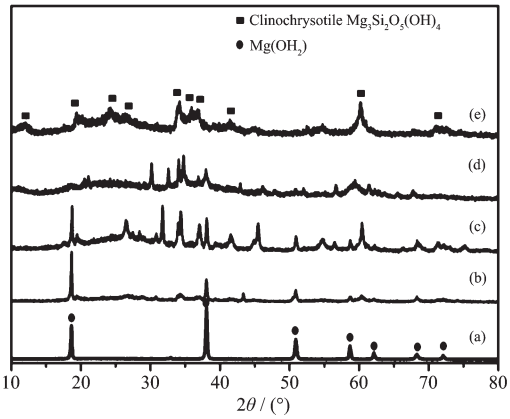
The proper composite hydroxides of potassium hydroxide and sodium hydroxide can form eutectic solution at lower temperature of 165 ℃, which presents a powerful system for synthesizing the complex oxide at ~200 ℃ or lower and normal atmosphere[30-31]. In this case, a combination of reagents was used to promote the formation of $Mg_3Si_2O_5(OH)_4$ nanotubes. A mixture of 1 g NaOH, 0.8 g KOH, 0.4 g $Mg(OH)_2$ and 0.4 g SiO_2 was placed in a 50 mL Teflon lined autoclave. The vessel was treated at 250 ℃ for 6 h at normal atmospheric pressure. After the vessel was taken out and cooled to room temperature, 30 mL deionized water was added to the solid precipitate (denoted as precursor-NK). Then the Teflon lined autoclave was sealed and hydrothermally treated at 250 ℃ and about 4 MPa for 30 h. The resulted $Mg_3Si_2O_5(OH)_4$ nanotubes (denoted as MS-NTs) were separated from the liquid phase by centrifuging and thoroughly washing with water. In a separate control experiment (traditional

method), the same mixture of 1 g NaOH, 0.8 g KOH, 0.4 g $Mg(OH)_2$, 0.4 g SiO_2, and 30 mL deionized water were directly put into a 50 mL Teflon lined autoclave. The Teflon lined autoclave was sealed and hydrothermally treated at 250 ℃ and about 4 MPa for 30~48 h. The solid products (denoted as MS-C30 and MS-C48 for hydrothermal treatment of 30 and 48 h, respectively) were recovered by centrifuging and thoroughly washed with water.

2　Results and discussion

Fig.1a, 1b and 1c show the XRD patterns of the starting material $Mg(OH)_2$, MS-C30 and MS-C48, respectively. One can easily find that after the traditional hydrothermal treatment of 30 h or even 48 h, there are still obvious peaks belonging to $Mg(OH)_2$, indicative of an incomplete conversion. Fig.1d shows the XRD pattern of the obtained solids after washing the precursor-NK with water, the main peaks of $Mg(OH)_2$ are almost disappeared, indicative of the almost complete conversion. The XRD pattern of the product MS-NTs (Fig.1e) can be readily indexed to clinochrysotile $Mg_3Si_2O_5(OH)_4$ (PDF No.21-1262), this monoclinic chrysotile is also a magnesium silicate hydroxide mineral of the serpentine group as first reported by Aristarain et al[32]. The lattice constants calculated from this XRD pattern are in good agreement with the reported values.

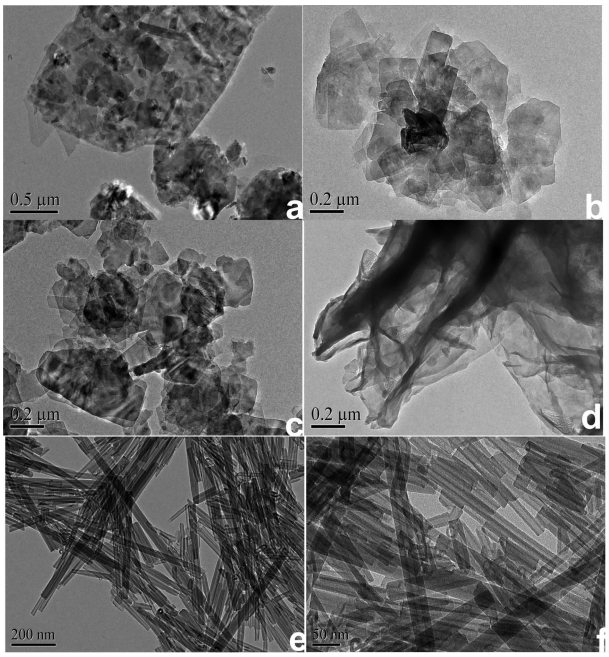
Fig.2a shows a typical low magnification TEM image of the starting material $Mg(OH)_2$. It appears that



(a) Starting material $Mg(OH)_2$, (b) MS-C30, (c) MS-C48, (d) precursor-NK and (e) MS-NTs

Fig.1　XRD patterns of the samples

the sample consists of irregular flakes with size from ~0.1 to several microns. The TEM images of MS-C30 and MS-C48 as shown in Fig.2b and 2c reveal that the flake morphologies of the samples are not changed after the traditional hydrothermal treatment for 30 h or even 48 h. Fig.2d shows a typical TEM image of the obtained solids after washing the precursor-NK with water. The gauze-like morphology obviously differs from that of the starting material $Mg(OH)_2$ and MS-C30/MS-C48, indicating the occurrence of conversion reaction. This result is in good accord with the XRD results. Fig.2e and 2d show typical images of the sample of MS-NTs observed with different magnifications. From these images one can see that all the samples possess uniform nanotube morphology with open ends. The obtained nanotubes have outer diameters of 30~50 nm, inner diameters of 8~20 nm, and lengths of 50 nm to more than one micrometer.

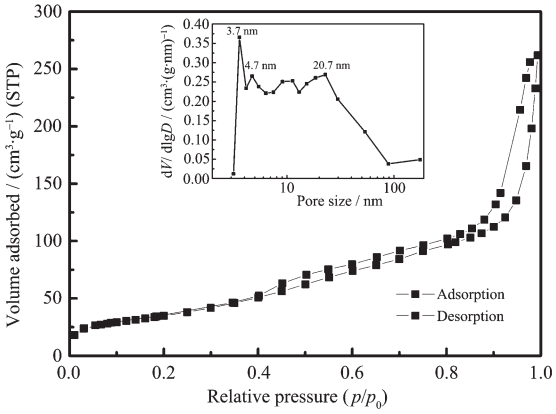


(a) Starting material $Mg(OH)_2$, (b) MS-C30, (c) MS-C48, (d) precursor-NK, (e) and (f) MS-NTs

Fig.2　TEM images of the samples

The surface area of the sample was calculated using a BET model, and the pore-size distribution was achieved using BJH model. The BET surface area of the obtained MS-NTs is 117 $m^2 \cdot g^{-1}$. As shown in Fig. 3, the magnesium silicate nanotube mainly contains mesoporous structure between 3.7 nm and 20.7 nm,

which is very close to that of the inner diameters shown in TEM images, indicating that most of the pores measured from the sample are tubular pores.



Inset: pore-size distribution curve obtained from the desorption data

Fig.3 N_2 adsorption/desorption isotherm of the MS-NTs

Fig.4 shows the FTIR spectra of MS-NTs. The peaks at 3 695 cm^{-1} and 3 568 cm^{-1} (shoulder) can be assigned to MgOH stretch. The peak at 1 640 cm^{-1} can be attributed to H_2O bend. The peak at 1 097 cm^{-1}, 1 000 cm^{-1}, 947 cm^{-1} can be assigned to Si-O-Si stretch, Si-O-Mg stretch, Si-O stretch, respectively. While the peak at 602 cm^{-1}, 446 cm^{-1}can be attributed to Mg-OH libration, Si-O-Mg bend, respectively. These results agree well with literature data for chrysotile ($Mg_3Si_2O_5(OH)_4$)[33], and confirm the chrysotile phase of MS-NTs.

Based on the above results, the synthesis of magnesium silicate nanotubes cannot be achieved by the traditional hydrothermal synthesis under mild conditions of 250 ℃ and about 4 MPa for a long time

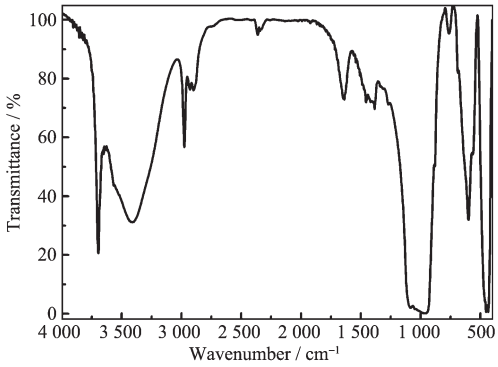


Fig.4 FTIR spectrum of the MS-NTs

of 48 h because of the low reactivity of the starting materials (solid Mg $(OH)_2$ and SiO_2). Under this mild conditions, the starting material $Mg(OH)_2$ is not reacted completely, not to mention converting to magnesium silicate nanotubes. In fact, even the reaction time is extended to 7 d, there still exists incomplete conversion. As shown in Fig.5, the XRD pattern of the product shows distinct peaks which do not belong to $Mg_3Si_2O_5(OH)_4$, and the representative TEM image reveals that there are obvious powders coexisted with one-dimensional nanotubes. These results accord well with the common conclusion of many reported investigations that the traditional hydrothermal synthesis of $Mg_3Si_2O_5(OH)_4$ nanotubes from normal SiO_2 and MgO/$Mg(OH)_2$ powders needs to be implemented at higher temperature and pressure, generally at 300~400 ℃ and 30~100 MPa.

Although the melting points of both pure sodium hydroxide and potassium hydroxide are over 300 ℃ (323 ℃ for NaOH and 360 ℃ for KOH), the eutectic point for NaOH/KOH of *ca.* 51.5∶48.5 is only about

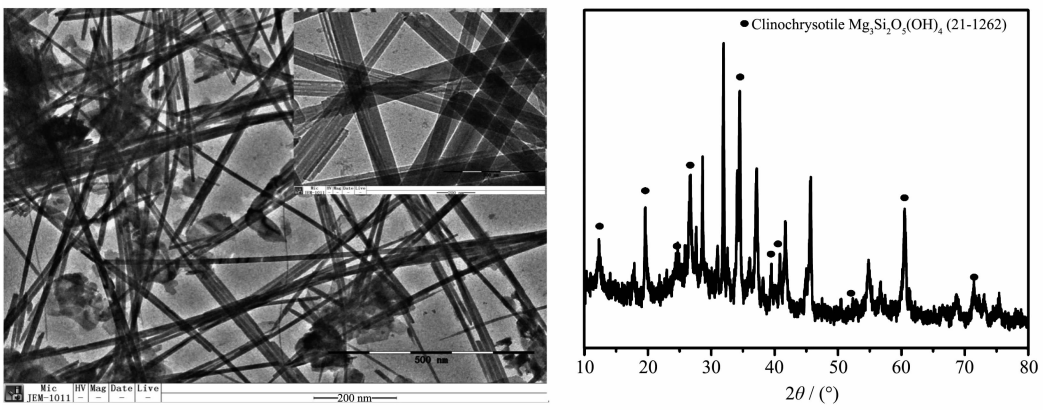


Fig.5 TEM image and XRD pattern of the sample obtained by traditional hydrothermal treatment for 7 d at 250 ℃

165 ℃[30-31]. With the assistance of the eutectic solution of potassium hydroxide and sodium hydroxide under 250 ℃ and normal atmosphere for a short time of 6 h, the starting materials $Mg(OH)_2$ and SiO_2 are effectively converted to the gauze-like precursor of $Mg_3Si_2O_5(OH)_4$. In general, metal hydroxides/oxides are soluble in basic composite hydroxides melts[30-31], which may contribute to the high reactivity of Mg $(OH)_2$. High dissolvability of hydroxide melts is beneficial not only to the dissolution of the reactants, but also to reaction between the reactants, which leads to the easy conversion of $Mg(OH)_2$ and SiO_2. In the molten hydroxides, SiO_2 reacts with NaOH/KOH and forms a hydroxide-soluble Na_2SiO_3/K_2SiO_3. For chemical reactions in the context, only NaOH is included in the formula for simplicity:

$$2NaOH+SiO_2 \rightarrow Na_2SiO_3+H_2O \quad (1)$$

The Na_2SiO_3 reacts with $Mg(OH)_2$ to form an indissoluble solid precipitate (precursor-NK):

$$Na_2SiO_3+Mg(OH)_2 \rightarrow \text{precursor-NK}+NaOH \quad (2)$$

The resulted gauze-like precursors curl readily form clinochrysotile $Mg_3Si_2O_5(OH)_4$ nanotubes in the following highly basic hydrothermal environment of 250 ℃ and about 4 MPa for 30 h.

Composite-Hydroxide-Assisted approach to the synthesis of nanostructures of complex oxides has been reported. However, the previous studies mainly focus on the direct synthesis from the composite hydroxides melts, and the obtained nanostructures mainly are nanocubes, nanosheets, nanowires, nanorods, nanobelts, nanoparticles, etc. To the best of our knowledge, there have been no reports on nanotubes up to now. We combine the Composite-Hydroxide-Assisted approach and hydrothermal route to synthesize uniform $Mg_3Si_2O_5(OH)_4$ nanotubes (chrysotiles) under mild conditions (250 ℃ and 4 MPa) in a short duration, compared with the hardly any conversion of the starting materials by traditional hydrothermal method under 250 ℃ and 4 MPa for a longer period of time. Very recently, this novel, mild, and highly efficient method has also been adopted for the synthesis of other nanostructures of complex oxides, and has revealed its unique advantages for the synthesis of complex oxide nanotubes. We believe this approach will find many applications in the controllable synthesis of nanostructured complex oxides with novel properties and morphologies, and more studies based on this approach will be reported later.

3 Conclusions

In summary, clinochrysotile $Mg_3Si_2O_5(OH)_4$ nanotubes with uniform morphology have been prepared via a mild composite-hydroxide-assisted synthesis from $Mg(OH)_2$ and SiO_2 powders. The eutectic solution of potassium hydroxide and sodium hydroxide offers high dissolvability for the reactants and benefits the reaction between the reactants. Compared with the traditional hydrothermal method, this composite-hydroxide-assisted approach is a mild and highly efficient procedure. The gauze-like precursor can be formed easily, and the following converting process to nanotubes under mild hydrothermal treatment requires a short period of time.

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