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Synthesis of Basic Magnesium Chloride Whisker in MgO-HCl-H_2O System at Room Temperature

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The basic magnesium chloride whiskers were synthesized by using industrial magnesia calcined from magnesite and hydrochloric acid as raw materials. X-ray diffraction, scanning electron microscopy, fourier transform infrared and thermal gravimetric analysis were used to characterize the samples in terms of the composition and morphology. The phase form of $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (form 318) was confirmed. a possible reaction mechanism and growth mechanism were proposed, the growth units of phase form 318 were amorphous [Mg-$(OH)_2$] and anion coordination-polyhedra $[Mg\text{-}(OH)_5]^{3-}$ other than $[Mg\text{-}(OH)_6]^{4-}$ octahedra practically existed in system MgO-HCl-H_2O as a precursor, $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ can easily be transformed to $Mg(OH)_2$ whiskers by base NaOH treatment. This confirmed that the Cl anion was rather than the structure of the free in the basic magnesium chloride whiskers.

Key Words: Industrial magnesia, Basic magnesium chloride, Whiskers, Growth units.

INTRODUCTION

The basic magnesium salt whiskers including basic magnesium chloride ,sulfate, carbonate, borate, *etc*. whiskers. They have similar molecular structure and same function characteristics of the enhancement, flame retardant and filler application in engineering plastic[1]. The basic magnesium chloride whiskers with a general formula of $xMg(OH)_2{\cdot}yMgCl_2{\cdot}zH_2O$ (x = 2,3,5,9; y = 1; z = 1,2,3…..)[2,3] were discovered and applied in cement[4]. The basic magnesium chloride whiskers could generally be synthesized in a typical method by using magnesium oxide powder and magnesium chloride solution as raw materials[5-8]. It could also be synthesized by using magnesium chloride solution and $NH_3{\cdot}H_2O$, $Ca(OH)_2$, NaOH, CaO, as raw materials[2,9,10]. the phase form 318 with the formula $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ were one of the most important and fundamental phase form on which being extensive investigated[11]. A number of workers indicated that the crystal structure of the phase form318 in system MgO-$MgCl_2$-H_2O were a condensation of the MgO_6 octahedra with respect to the $Mg(OH)_2$ content and intercalated with chloride atoms/ions and water molecules[5,11]. $Mg(OH)_2$ nanotubes can be synthesized by using $Mg_{10}(OH)_{18}Cl_2{\cdot}5H_2O$ nanowires as precursors and rod-like $Mg(OH)_2$ prepared by basic magnesium chloride precursor[12]. In this paper, the phase form 318 were synthesized in system MgO-HCl-H_2O and the amorphous magnesium hydroxide [Mg-$(OH)_2$], Mg^{2+} and Cl^- ions, $[Mg\text{-}(OH)_5]^{3-}$ anion coordination-polyhedras[13] and H_2O were proposed as the basic growth units to form the phase form 318 basic magnesium chlorides whiskers according to the experiment of the dissolution of MgO and $MgCl_2$ in water and the coordination reaction of ions Mg^{2+} and OH^- [3]. The fact of the basic magnesium chloride wkiskers were then transformed into $Mg(OH)_2$ whiskers by base NaOH treatment confirmed that the Cl anions were rather than the structure of the free in the basic magnesium chloride wkiskers.

EXPERIMENTAL

Industrial magnesia calcined from magnesite (Table-1), Hydrochloric acid 37 wt. % (AR) and NaOH (AR) were used as raw materials. The basic magnesium chloride whiskers were synthezed in the system MgO-HCl-H_2O, 200 mL 8 mol/L hydrochloric acid was poured into a flask-3-neck placed in a constant temperature bath at 50 °C, added magnesite into the hydrochloric acid solution slowly, the molar ratio of the magnesite to hydrochloric acid was 0.625:1. stired the mixture for 2 h, then filtered the insoluble impurities immediately, the filtrate was left to stand at room temperature for 2 days, collected the precipitation and washed with deionized water and ethanol, respectively. and then vacuum dried under the condition of 50 °C for 4 h. Mix the obtained samples and NaOH solution uniformly then stirred and kept at 70 °C for 2 h. The product $Mg(OH)_2$ precipitation was filtered and washed with water and ethanol, respectively. then vacuum dried at 70 °C for 4 h. Finally, the $Mg(OH)_2$ whisker was obtained.

TABLE-1
COMPOSITION OF MAGNESITE

Composition		Elements				
		O	Mg	Ca	Fe	Si
Content	W %	42.33	54.39	1.08	0.51	1.7
	A %	53.13	44.93	0.54	0.18	1.21

RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns of obtained samples by Bruker D8 Advance X-ray diffractometer. The results indicated that the peak compositions of the samples are consistent with the standard diffraction pattern of the basic magnesium chloride (JCPDS 07-0412) with a formula of $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, The diffraction peaks at 2θ values of 11, 12.5, 15, 22, 23, 25, 29.5 and 37 are corresponding to (100), (001), (101), (200), (201), (002), (102) and (202) planes of the crystaline structure of the basic magnesium chloride respectively.

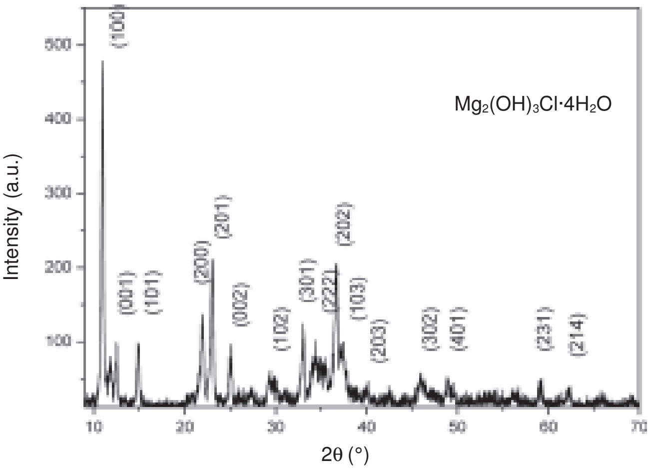

Fig. 1. XRD patterns of samples obtained in system $MgO-HCl-H_2O$

The fourier transform infrared spectra were used to investigate the composition of theobtained samples. Fig. 2 shows the FTIR spectrum of the obtained sample. the absorption band at 3441 cm^{-1} is the characteristic frequency of the hydroxyl group (OH) stretching vibration. a sharp peaks at 3656 cm^{-1}, 3638 cm^{-1} and 1630 cm^{-1} are the absorption band of crystal water in basic magnesium chloride. the absorption band at 1160 cm^{-1} is the bending vibration band of the coordinate of OH- accordingly.

Fig. 3 shows the SEM images of the obtained samples. It indicated that the obtained samples have a morphology of whisker with a diameter of 200-500 nm. and a length of 20 µm or more.

Fig. 4 shows the TGA of the obtained samples as prepared, the thermal decomposition of obtained samples proceed *via* dehydration (removal of crystal water) below 310 °C, dehydroxylation occured between 310 °C and 520 °C. The total theoretical mass loss of water expected in phase form 318 was 55.1 % including a theoretical mass loss of 34.95 % (below 310 °C) and 20.16 % (at 520 °C left and right). The experimental total mass loss of TGA nearly reached 57 %, the results confirmed that the obtained samples in the system $MgO-HCl-H_2O$ was phase form 318 construction.

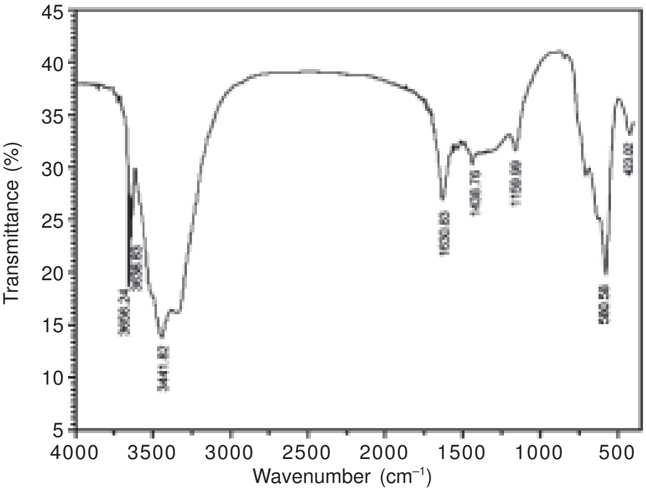

Fig. 2. FTIR spectrum of the obtained sample

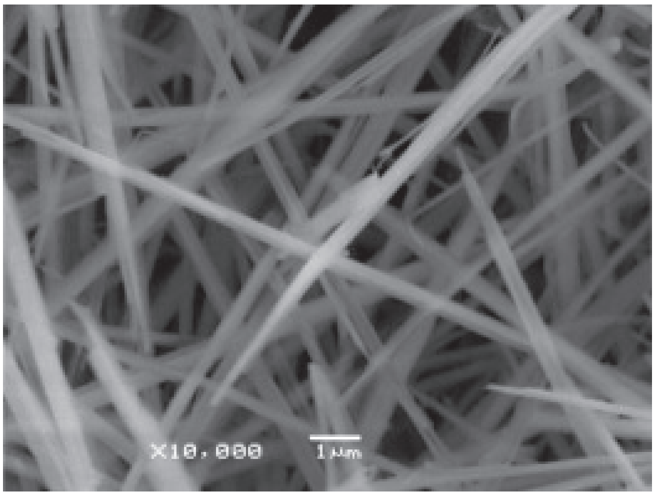

Fig. 3. SEM images of the obtained samples

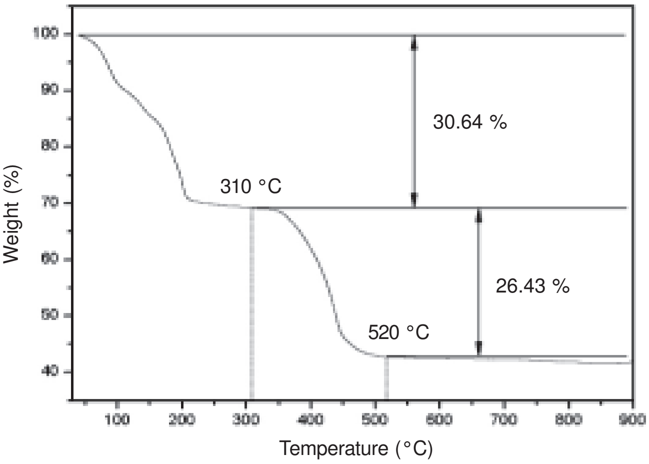

Fig. 4. TGA of the obtained samples

The reaction mechanism of the process can be divided into two parts, one part was that metal oxide in magnesite including MgO, CaO and Fe_2O_3 firstly reacted with hydrochloric acid, then transform into $MgCl_2$, $CaCl_2$, $FeCl_3$ and the second was that the rest of the MgO in the solution reacted with $MgCl_2$ and then transformed into basic magnesium chloride whiskers. the equations can be seen as eqns. 1 and 2.

$$\begin{gathered} MgO + 2HCl \longrightarrow MgCl_2 + H_2O \\ CaO + 2HCl \longrightarrow CaCl_2 + H_2O \\ Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O \end{gathered} \quad (1)$$

$$3MgO + MgCl_2 + 11H_2O \rightarrow 3Mg(OH)_2{\cdot}MgCl{\cdot}4H_2O \quad (2)$$

The insoluble impurities were filtered immediately from the mixture, the filtration then left at room temperature for 48 h, the white prepcipitate would produced, filtrate cake were obtained samples and the soluble reactants including $MgCl_2$, $CaCl_2$ and $FeCl_3$ transfered into the filtration.

The growth mechanism for phase form 318 were proposed that the process of activity magnesium oxide dissolved in water includes dissolution, hydration, transformation, aggregation, gelatination and disaggreagation can be seen in eqn. 3. The dissolution of magnesium chloride produced in water were fast and easily, the acidity of strong acid salt express out in a short time as eqn. 4. The crystallization growth units of phase form 318 in the system of MgO-$MgCl_2$-H_2O included amorphous $[Mg\text{-}(OH)_2]$, Mg^{2+}, Cl^-, H_2O and $[Mg\text{-}(OH)_5]^{3-}$ as eqn. 5, it was proposed that the growth unit for form 318 were amorphous $[Mg\text{-}(OH)_2]$ and anion coordination-polyhedras[13] $[Mg\text{-}(OH)_5]^{3-}$ other than $[Mg\text{-}(OH)_6]^{4-}$ octahedra practically existed in the solution[3].

$$MgO + H_2O \rightarrow MgO{\cdot}H_2O \rightarrow Mg(OH)_2 \rightarrow [Mg\text{-}(OH)_2] \rightarrow x[Mg\text{-}(OH)_2] \quad (3)$$

$$MgCl_2 + H_2O \rightarrow Mg^{2+} + 2Cl^- + 2H^+ + 2OH^- \quad (4)$$

$$3[Mg\text{-}(OH)_2] + 8H^+ + 3OH^- + 2Cl^- + [Mg\text{-}(OH)_5]^{3-} \rightarrow 3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (5)$$

Fig. 5 shows the XRD patterns of $Mg(OH)_2$ which was transformed by base NaOH treatment. The results indicated that the peak compositions of the samples are consistent with the standard diffraction pattern of magnesiumhydrate $Mg(OH)_2$ (JCPDS 07-0239). And Fig. 6 shows the SEM images of the samples, the results show that the whisker shape maintained still very well in the $Mg(OH)_2$. The fact of the basic magnesium chloride wkiskers can be transformed into $Mg(OH)_2$ whiskers by base NaOH treatment provided an evidence of that the Cl anions were rather than the structure of the free in the basic magnesium chloride wkiskers[2,5,8].

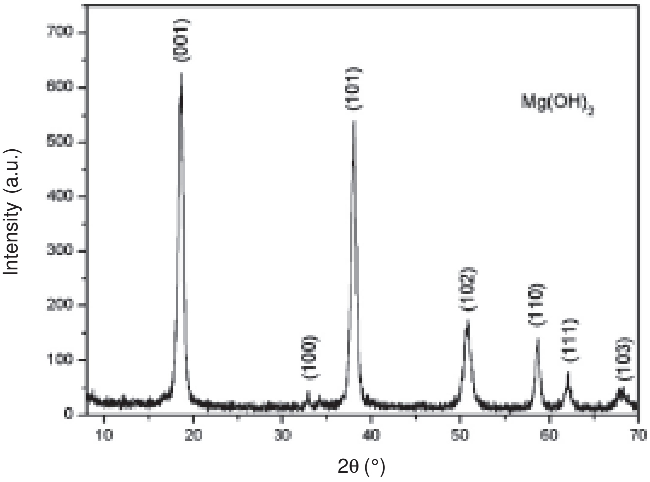

Fig. 5. XRD patterns of $Mg(OH)_2$ samples

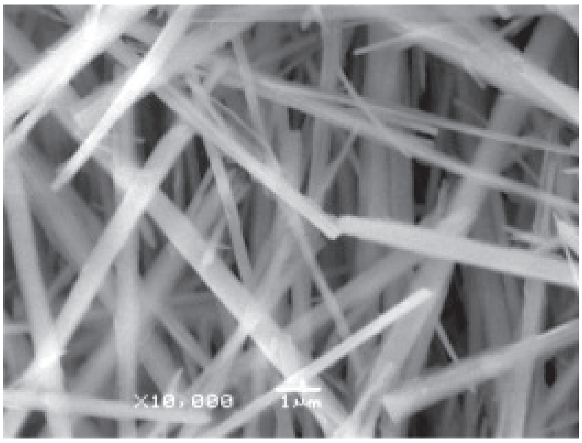

Fig. 6. SEM images of the $Mg(OH)_2$ samples

Conclusion

The basic magnesium chloride whisker was firstly synthesized in the system MgO-HCl-H_2O at room temperature. XRD, SEM, FTIR and TGA analysis confirmed that the phase form of $3Mg\ (OH)_2{\cdot}\ MgCl_2{\cdot}8H_2O$ (form 318) were obtained. it was proposed that the growth unit of phase form 318 were amorphous $[Mg\text{-}(OH)_2]$ and anion coordination-polyhedras $[Mg\text{-}(OH)_5]^{3-}$ other than $[Mg\text{-}(OH)_6]^{4-}$ octahedra practically existed in the MgO-HCl-H_2O. $Mg(OH)_2$ whiskers could be made by using phase form 318 as precursor. The transformation provided an evidence of that the Cl anions were rather than the structure of the free in the basic magnesium chloride wkiskers.

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