Synthesis of Spherical Magnesium Lithium Silicate Using Natural Brine

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Abstract: Spherical nanoparticles of Magnesium Lithium Silicate were synthesized hydrothermally using natural brine of Qaidam Salt Lake as starting materials. The concentrated brine was utilized directly without separating lithium or magnesium from brine at first. It is a good idea to make use of the salt lake resources in this region. The samples were determined by X-ray and TEM. The surface area and particle size were calculated.

Key words: Hectorite; Nanoparticle; Brine; Clay; Magnesium Lithium Silicate

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0 Introduction

Magnesium Lithium Silicate ($Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2$), Hectorite is a sort of layered smectite. Smectites are valuable minerals in industry. Because they have high cation exchange capacities, surface area, surface reactivity, adsorptive properties, intercalation and swelling properties, they are applied as host materials for transition metals and metal complex catalysts. Hectorite is a trioctahedral analog of montmorillonite with substitution of Li for Mg in the octahedral sheet and some Al for Si in the tetrahedral sheet. It is rare mineral clay and explored only in American. The material is attracting considerable interest in polymer science research, and the most of the smectite-type layered silicates were commonly used for the preparation of nanocomposites [1-3]. Hectorite has a lot of properties, especially with high viscosity and transparency in solution [4-6]. It is also used in lithium-ion batteries.[7-9]

It is well known that there are a lot of salt lakes in China's northwestern area, many of which contain an abundance of lithium, magnesium, potassium, sodium, boron, cesium and many other elements. Some of the elements play an important role in IT, agriculture and other fields. The Qaidam Basin is located in Tibetan Plateau of China. There is abundance of resources in Qaidam Salt Lakes, for example, lithium (LiCl) is 0.01%~0.12%, magnesium ($MgCl_2$) is 1.61%~27.45%, potassium (KCl) is 0.07%~2.86%, sodium (NaCl) is 1.40%~23.85%, boron (B_2O_3) is 0.004%~0.36%, etc [10]. For a long time, scientists have been investigating and exploring how to separate lithium and magnesium from brines, until now there is not any available technology to extract lithium from brines, because the ratio of Mg/Li is higher than that other salt lakes, from 40:1 to 1 200 :1. In this paper, we will utilize this brine to prepare Magnesium Lithium Silicate (Hectorite) without separating

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lithium or magnesium from brine firstly.

1 Experimental

1.1 Preparation of concentrated brines

In the salt lakes of the Qaidam Basin, the solid phase in the sediments contains principally halite, gypsum and little carnallitite. Other important minerals exist in brine. After isothermal and solar evaporation of brine, halite and carnallitite are precipitated in solar ponds. After further evaporation of brine, the carnalliitite is precipitated in solar ponds. We can get the concentrated brine, Its chemical compose analysis is LiCl: 1.20%~2.50%, $MgCl_2$: 28.60% ~ 29.13%, KCl: 0.18% ~ 0.28%, NaCl: 1.42%~1.82%, B_2O_3: 1.66%~1.76%, $MgSO_4$: 3.25% ~ 3.75%, H_2O: 61.37% ~ 63.09% [10-13].

1.2 Preparation of Hectorite

$Li(OH)\cdot H_2O$, LiF or $MgCl_2\cdot 6H_2O$, MgO and $Na_2SiO_3\cdot 9H_2O$ (Analytical grade, Beijing chemical Co.) were added into the concentrated brine. According to the chemical formula ($Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$), and the chemical analysis of the concentrated brine, the molar ratio of Mg^{2+} : Li^+ : Si^{4+} is 2.7:0.3:4 in this concentrated brine, and adjust the pH of the brine to 11 using the solution of NaOH. The mixtures were reacted by hydrothermal method.

All the hydrothermal reactions were carried out in a self-made Teflon-lined closed stainless steel autoclave which volume is about 50 mL. The reactor was put into oven which reached definite temperature in advance. After 20 h at 200±1 ℃, the reactor cooled naturally at room temperature. Crystallization of $Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$ was obtained by centrifugal sedimentation.

1.3 Characterization

The X-ray diffraction analysis was performed at room temperature to identify the crystalline phase of the powder with Cu Kα radiation on a X'Pert PRO X-ray diffractometer (PANalytical, Holland). The morphologies of the materials synthesized were studied by Hitachi H-6 000 transmission electron microscopy (TEM) (Hitachi, Japan).

The chemical analysis was performed to identify the chemical formula of the samples. The concentrations of Li^+, Na^+, K^+ and Si^{4+} were determined by atomic adsorption spectroscopy (AAS) (GBC 908, GBC Co., Australia).

Magnesium was titrated by a standard solution of Na-EDTA in an alkaline buffer solution of ($NH_3 + H_2O + NH_4Cl$), boron by a standard solution of NaOH in the presence of mannitol, and H_2O by difference method.

Impurity elements were detected by the Axios XRF (X-Ray Fluorescence) Spectrometer (PANalytical, Holland).

2 Results

The concentrated brine contained LiCl: 2.50%, NaCl: 1.42%, KCl: 0.18%, $MgCl_2$: 29.13%, $MgSO_4$: 3.75%, B_2O_3: 1.66%, H_2O: 61.37% and a small quantity of other impurity elements. After synthesized hydrothermally, the solid samples contained Na_2O: 3.23%, Li_2O: 1.17%, MgO: 28.39%, SiO_2: 62.71%, H_2O: 4.70%. Impurity elements were Al: 0.06%, S: 0.006%, Cl: 0.115%, K: 0.021%, Fe: 0.018%. The chemical formula of the compound is $Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$.

X-ray diffraction pattern (Fig.1) showed that the sample was layered smectite clay. The parameter was $a=5.2$, $b=9.16$, $c=16.0$, $\beta=\sim 99°$, Monoclinic, C2/m.

Fig.2 showed that $Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$ was spherical nanoparticles. From X-ray diffraction pattern (Scherrer formula, $D=K\lambda/B_{1/2}\cos\theta$), we can get the size of average spherical nanoparticles is

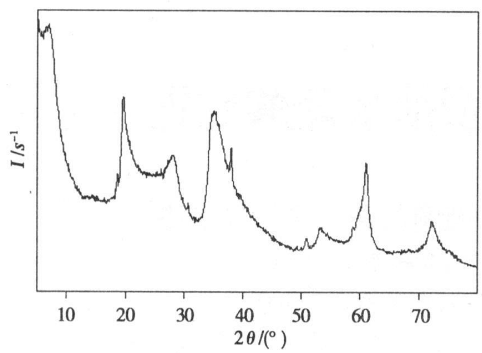

Fig.1 X-ray diffraction pattern of $Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$

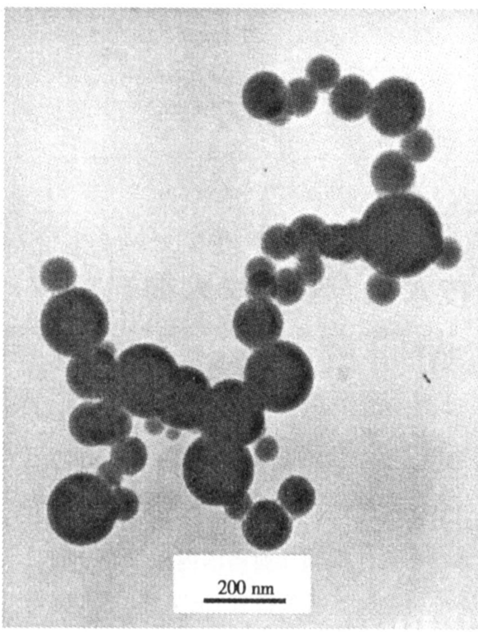

Fig.2 TEM of $Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$

$D_{(100)}\cong 4$ nm. The surface area can be calculated by $s=6/\rho D\times 6.5\times 10^4$ m^2/g, where ρ is the calculated density of Hectorite, about 2.3 g/cm^3, D is the average crystallite size, the Scherrer constant K is assumed to be to 1, λ is the wavelength of the radiation (usually 0.154 056 nm for Cu $K\alpha_1$), $B_{1/2}$ is the integral breadth at half maximum of a reflection (in radians 2θ). From TEM the spherical nanoparticles size was below 200 nm.

Hectorite spherical nanoparticles were hydrothermally synthesized using natural brine of Qaidam Salt Lakes as starting materials. The concentrated brine was utilized directly without separating lithium or magnesium from brine firstly. This is a good idea to develop and utilize the salt lake resources in this region.

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由盐湖卤水合成球形纳米硅酸镁锂

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摘　要：用青海柴达木盆地的盐湖卤水为原料，经浓缩后用水热法直接合成球形纳米硅酸镁锂，此方法充分利用了盐湖资源，无需镁锂分离。同时对样品进行了X－ray、TEM表征、计算了比表面积和粒径。

关键词：锂皂石；纳米材料；卤水；粘土矿物；硅酸镁锂
