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Research paper

Comprehensive use of dolomite-talc ore to prepare talc, nano-MgO and lightweight $CaCO_3$ using an acid leaching method

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ABSTRACT

The talc powder associated with dolomite, from Luonan county, Shaanxi province, China, was leached with 2.25 mol hydrochloric acid (37%) to obtain $MgCl_2$–$CaCl_2$ solution and purified talc powder. The iron cations in the solution were removed by adding 9% sodium hypochlorite as an oxidant, and adjusting the solution pH to 7. Magnesium hydroxide was obtained after ammoniation of the solution using 26% ammonia until pH above 12. Magnesium oxide nanoparticles were prepared by calcining the magnesium hydroxide at 800 °C for 4 h. Then, CO_2 gas, at concentrations of either 40% or 99.9%, was bubbled through the $CaCl_2$–NH_4Cl solution, to form aragonite or vaterite, respectively. This work mainly investigates the effect of molar volume of the hydrochloric acid on dolomite solution, the effect of pH on the Mg^{2+} precipitation yield, the effect of calcination temperature on the average grain size and morphology of the MgO particles, and the effect of CO_2 gas concentrations on the calcium carbonate crystal polymorphs. Scanning electron microscopy, X-ray diffraction and chemical analysis methods were used to characterize the products. The magnesium oxide nanoballs formed, with average particle size of 80–100 nm and purity of 99.14%, can be used in catalysis, as refractory materials, and in a range of other applications. The purities of both aragonite and vaterite were above 98%, and both products gave whiteness values over 96%. The technique presented in this work, which features low energy consumption and high use ratio, is a potential environmentally friendly way for clean processing of low-grade dolomite-talc ores.

1. Introduction

Talc rock is produced by hydrothermal metamorphism of magnesium ultramafic rocks and dolomite, and is widely used in many fields. Commercially exploited talc rocks usually contain 20–90% talc mineral. Although effective processing methods have been developed for the higher-purity ores, suitable methods for processing low-grade talc have not been developed and applied industrially. A large amount of low-grade dolomite-talc is distributed throughout the world (Shin and Lee, 2003). Therefore, approaches to exploit low-grade dolomite-talc will be required as the higher-grade deposits become depleted.

Dolomite is commonly associated with talc. Current processes to use dolomite are primitive and energy-intensive (Yildirim and Akarsu, 2010; F.F. Zhang et al., 2012; K.Q. Zhang et al., 2012). The carbonation method, the second carbonization method, and the double-loop method involving carbon dioxide and ammonia have all been adopted worldwide to prepare magnesium oxide and calcium carbonate products from dolomite (Boonyawan et al, 2011; Galai et al., 2007; Rodriguez-Navarro et al., 2012; Yildirim and Akarsu, 2010). However, all these methods require calcination of raw materials, which consumes a large amount of energy. Coal is the main source of energy in China, and burning of coal can be a major source of environmental pollution. This makes finding a green and environmentally friendly way to process dolomite essential. At present, the preparation of magnesia and calcium carbonate by direct chemical precipitation from dolomite is just in its infancy.

Based on this, we have used dolomite-talc from Luonan in China as the raw material in this study; the dolomite-talc powder is directly leached into hydrochloric acid during chemical purification, to leave high purity talc (which is insoluble under the conditions used). The acid leaching solution contains $CaCl_2$ and $MgCl_2$. Magnesium hydroxide is then synthesized by ammoniating the $CaCl_2$–$MgCl_2$ solution; nano-magnesium oxide can then be obtained simply by calcining the magnesium hydroxide sample. Subsequently, CO_2 gas at concentrations of either 40% or 99.9% is bubbled through the remaining $CaCl_2$–NH_4Cl solution. Two polymorphs of lightweight calcium carbonate were obtained at different CO_2 concentrations. Our experiments explored the influence of pH on the yield of Mg^{2+} precipitation during the ammoniation process, the influence of calcination temperature on the average grain size and morphology of the MgO particles formed, and the influence of CO_2 gas concentration on the morphology and polymorph of calcium carbonate formed during the carbonation process.

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Table 1
Chemical composition of Luonan talc (w_B%).

Sample	SiO_2	TiO_2	Al_2O_3	TFe	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O^-	LOI
LT10	22.92	0.063	1.64	0.52	0.015	23.20	19.29	0.38	1.03	0.011	0.052	30.94

2. Materials

The average particle size of the dolomite-talc powder used as raw material is 24 μm. The whiteness of Luonan talc rock is 93.24% (ISO Brightness). The chemical composition and X-ray diffraction analysis results for the talc ore are presented in Table 1 and Fig. 1.

The main phases of the talc ore samples can be determined from X-ray powder diffraction. These phases are talc (PCPDF NO.19-0770), dolomite (PCPDF NO.36-0426), quartz (PCPDF NO.83-2468), and phlogopite (PCPDF NO.10-0495). Based on mass balance principle, the mineral content of the talc ore was calculated from its chemical composition and its major phases. The ore includes 30.06 wt.% talc, 62.09 wt.% dolomite, 3.87 wt.% quartz and 3.98 wt.% other minerals (Li et al., 2011).

3. Experimental principle and methods

3.1. Experimental principles

Dolomite is a carbonate mineral, with a crystal chemical formula of $CaMg[CO_3]_2$, which can react with hydrochloric acid which concentration is 37% to produce $MgCl_2$–$CaCl_2$ solution. Pure talc, which is insoluble in hydrochloric acid, was also obtained. The final talc product, which had a purity of 96% and whiteness of 90.75%, can be used as a filler in rubbers and cosmetics.

Mg^{2+} and Ca^{2+} concentrations in the solution are 1.115 mol/L and 1.399 mol/L, respectively. The $MgCl_2$–$CaCl_2$ solution contains small amounts of impurities such as Fe^{3+} and Fe^{2+}ions, and needs purification. Fe^{2+} and Fe^{3+} concentrations in the solution are 2.28 × 10–4 mol/L and 1.4 × 10–5 mol/L, respectively. The pH values where different metal hydroxides precipitate were calculated using the solubility constants and the ion concentrations in solution at room temperature (Table 2) (Lide, 2003).

The calculations in Table 2 show that the pH values for $Fe(OH)_2$ and $Mg(OH)_2$ precipitation are close to each other. Therefore, they cannot be easily separated by precipitation. $Fe(OH)_2$ can be oxidized to $Fe(OH)_3$ using 9% NaClO as an oxidant, and then adding ammonia dropwise into the acid solution to give a pH value of 7. The Fe^{3+} ions in the solution generate precipitation. Pure $MgCl_2$ and $CaCl_2$ solution is obtained after filtration.

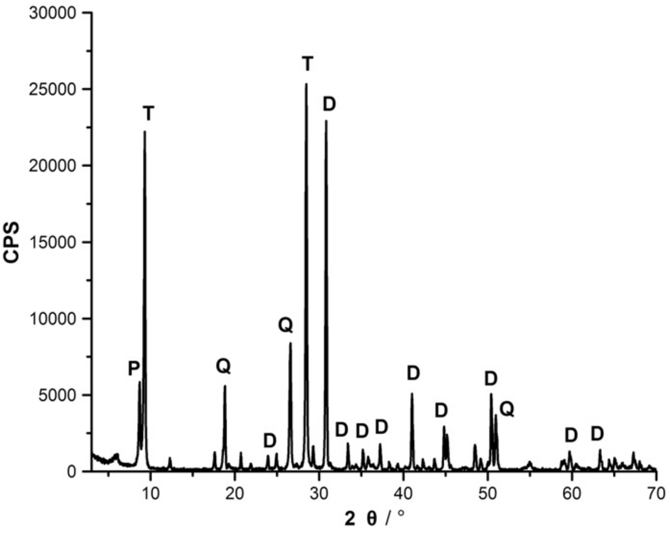

Fig. 1. X-ray powder diffraction pattern of Luonan talc ore (T: talc; D: dolomite; Q: quartz).

The ammoniation reaction involves adding 26% ammonia dropwise into the pure $MgCl_2$–$CaCl_2$ solution. According to Table 2, adjusting the pH above 8 can convert most of Mg^{2+} in the solution into $Mg(OH)_2$ precipitate. Ca^{2+} ions remain in the solution after filtration. The separation of calcium and magnesium occurs at that moment when the extraction rate of magnesium is 98.7%. Magnesium oxide powder is obtained after calcination of magnesium hydroxide.

The CO_2 gas is then blown into the solution, which contains $CaCl_2$–NH_4Cl. The Ca^{2+} ions react with the CO_2 to form $CaCO_3$.

The main chemical reactions that occurred in this research were:

$$CaMg[CO_3]_2 + 4HCl \rightarrow MgCl_2 + CaCl_2 + 2H_2O + 2CO_2 \tag{1}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3\downarrow \tag{2}$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3\downarrow \tag{3}$$

$$Mg^{2+} + 2NH_3 \cdot H_2O \rightarrow Mg(OH)_2\downarrow + 2NH_4^+ \tag{4}$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \tag{5}$$

$$Ca^{2+} + 2OH^- + CO_2 \rightarrow CaCO_3\downarrow + H_2O. \tag{6}$$

3.2. Experimental procedure

The experimental route used in this research was shown in Fig. 2.

3.3. Experimental method

The chemical compositions of the prepared samples were determined by wet chemical analysis. The solid products synthesized were identified by powder X-ray diffraction (XRD), performed on a Rigaku D/Max-2500 diffractometer with Cu *Kα* radiation. Data were collected over a 2θ range of 3° to 70°, with a step size of 0.01°. Surface morphology was investigated using a Hitachi S-4800 scanning electron microscope. The whiteness value determination was carried out on YQ-z-48B whiteness meter instrument under D65 illuminant with whiteness mean of R457.

Table 2
The pH needed to precipitate different hydroxides at 25 °C.

	Ksp	pH value of the precipitate formation
$Ca(OH)_2$	5.02×10^{-6}	11.3
$Mg(OH)_2$	5.61×10^{-12}	8.35
$Fe(OH)_2$	4.87×10^{-17}	7.66
$Fe(OH)_3$	2.79×10^{-39}	2.1

Note: Mg^{2+} and Ca^{2+} concentrations in the solution are 1.115 mol/L and 1.399 mol/L, respectively. Fe^{2+} and Fe^{3+} concentrations in the solution are 2.28×10^{-4} mol/L and 1.4×10^{-5} mol/L, respectively.