

Preparation of nano-structured strontium carbonate from Dasht-e kavir celestite ore via mechanochemical method

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Received: 28 October 2017; Accepted: 28 April 2018

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ABSTRACT

In the present investigation, nano-structured strontium carbonate was synthesized by mechano-chemical reaction of raw mineral celestite ore (SrSO_4) collected from Dasht-e kavir, Iran, without initial acid leaching and chemical beneficiation, and sodium carbonate during high energy mechanical milling. X-Ray diffraction (XRD), X-ray fluorescence spectrometer (XRF), atomic absorption spectroscopy (AAS) and scanning electron microscope (SEM) were used to characterize the obtained samples. XRD results showed that at a $\text{Na}_2\text{CO}_3:\text{SrSO}_4$ molar ratio of 1.05:1, mechano-chemical reaction started after 1 hour of milling. Although the longer milling times gives a more conversion of SrSO_4 to SrCO_3 but it has not been completed even after 16 hours of milling. However, by increasing the molar ratio of $\text{Na}_2\text{CO}_3:\text{SrSO}_4$ to 1.25:1, the SrCO_3 formation was completed after 2 hours. The results also showed that the mean crystallites sizes of produced nano-powder were approximately 32 nm. XRF result indicated that the final product was obtained with a purity of 95 wt.%. AAS results specified that the recovery rate for production of SrCO_3 from celestite concentrate was about 97%. SEM studies confirmed the formation of SrCO_3 nano-powder with a mean particle size of 80 nm.

Keywords: Strontium carbonate; Celestite ore; Nano-structured; Mechanochemical.

1. Introduction

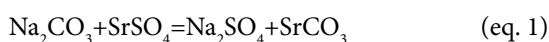
Strontium carbonate (SrCO_3) is one of the most important strontium compounds that have been used in a variety of technological and industrial applications. It is particularly used as an additive in the fabrication of glass cathode-ray tubes for TV and computer monitors (more than 65% of total production) and as a constituent of magnetic ferrites (more than 20% of total production). Other applications are in the manufacturing of special glasses, in pyrotechnics, paints, medicine and photocatalysts such as strontium titanate and zirconate for aqueous degradation of organic pollutants and advanced ceramic materials. Although SrCO_3 occurs naturally as mineral

strontianite, most of it that is available has been produced from celestite ore (SrSO_4) that is the only commercially exploited strontium mineral [1-3].

There are two commercial processes to manufacture SrCO_3 from celestite; the black ash and the double decomposition (direct conversion) processes. In the black ash process, SrSO_4 is reduced with coke (or coal) at temperatures generally over than 1000 °C to produce water soluble SrS. The sulfide is then leached in hot water and strontium carbonate is precipitated using soda ash, ammonium bicarbonate and/or CO_2 [4-7]. In the second process, finely powdered celestite is reacted with hot sodium carbonate solution (>90 °C) to obtain SrCO_3 and by-product sodium

sulfate by a double decomposition reaction. Although the black ash method produces a higher purity SrCO₃ product, it is more energy intensive than the double decomposition process [8-11]. Beside the two above commercial methods, there are several reports of the conversion of celestite to SrCO₃ by other methods including the high temperature and high-pressure reaction between celestite and either sodium or potassium carbonate and direct leaching of celestite with Na₂S to produce SrCO₃[12].

During the last few years, application of mechanical milling to induce solid-state reactions, reduction of metal oxide to metallic materials, synthesis of nanoparticles and composite materials have been widely studied. Erdemoglu [13] studied on the kinetics of the conversion of celestite to SrCO₃ by mechano-chemical processing under wet milling conditions by varying the amount of sodium carbonate with respect to the stoichiometric amount required for the conversion reaction. The celestite reacts with sodium carbonate giving solid strontium carbonate and soluble sodium sulfate, according to the following reaction (eq. 1).



Zhang and Saito [14] prepared SrCO₃ indirectly by carbonation of Sr(OH)₂ which was produced by dry high-energy milling of celestite and NaOH in a planetary ball mill. Obut et al. [15] prepared SrCO₃ from celestite concentrate using both solid and aqueous sodium carbonate in a planetary ball mill and showed that 93% conversion of SrCO₃ could be obtained after 40 min milling. Further experiments showed that the best conversion of celestite to strontianite occurs during dry milling. These results are very interesting since they demonstrated a direct solid-state conversion of SrSO₄ to SrCO₃ and a further examination of dry milling is warranted.

The aim of this work is to evaluate the influence of the Na₂CO₃:SrSO₄ molar ratio and milling time

on the synthesis of SrCO₃ nano-particles from celestite natural ore by mechanical milling in a systematic manner. To the best of our knowledge, there is no work that has been reported on the production of the strontium carbonate with a good purity from the low cost celestite mineral obtained from Dasht-e kavir mine. Specially, starting material of celestite ore without initial acid leaching and chemical beneficiation will make the process more economical to produce strontium carbonate with a good purity as compared to the use of high purity starting materials. Also a detailed understanding of the preparation process is crucial in order to control the morphology and structure of the produced nano-powder for the desired applications.

2. Materials and methods

celestite concentrate with a particle size range of 100–500 μm beneficiated by shaking table supplied from Dasht-e kavir mine, Iran (96% SrSO₄, 2% CaCO₃, 1% BaSO₄ and 1% other impurities) and Na₂CO₃ (98% purity) were used as the starting materials. The milling experiments were performed for different durations of time up to 16 hours and various Na₂CO₃:SrSO₄ molar ratios of 1.05:1, 1.15:1 and 1.25:1 in a high-energy planetary ball mill (PM2400 model) with hardened steel chamber and balls 15 mm in diameter, under air atmosphere. The rotational speed and ball to powder weight ratio were 300 rpm and 30, respectively. The milled samples were washed with water to remove the produced Na₂SO₄ phase during reaction to obtain a pure SrCO₃ nano-powder. Na₂SO₄ leached by neutral water with the pH of 7 (solid/liquid ratio=1:30 g/mL, ambient temperature ~20 °C, time=30 minutes, stirring speed=300 r/min). Then, the solid and the liquid phases were separated, and the solid product was dried at 110 °C. The flowchart of the experimental work is shown in Fig. 1.

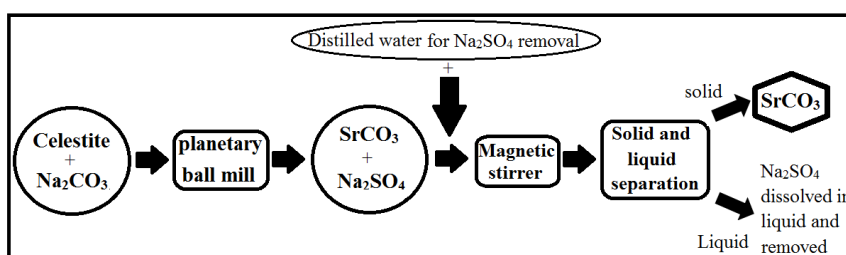


Fig. 1- Flowchart of the experimental procedure.

Philips PW-1730 X-ray diffractometer (XRD) using Cu K_α radiation (λ= 1.5405 Å) in the range of 20° ≤ 2θ ≤ 70° and step size of 0.02 was used for the structural characterization. The Oxford ED2000 model X-ray fluorescence spectrometer (XRF) and an atomic absorption spectrometer (AA spectrometer, UNICAM939) were employed for chemical analysis and evaluation of final purity of the product. The morphology of powders was examined by scanning electron microscope (SEM, TESCAN). The mean crystallite size of the samples was calculated from full-width at half maximum (FWHM) peak by the Williamson-Hall equation (eq. 2) [16]:

$$B \cos \theta = \frac{0.9\lambda}{D} + 4 \varepsilon \sin \theta \quad (\text{eq. 2})$$

Where D is the crystallite size, λ is the X-radiation wavelength, θ is the diffraction angle, β is the full width at half maximum and ε is the internal strain.

3. Results and discussion

Fig. 2 depicts the XRD patterns of the mixture before and after different milling times at the constant Na₂CO₃:SrSO₄ molar ratio of 1.05:1. The as-received celestite concentrate started to be converted into strontium carbonate after 1 hour of milling. As indicated in the figure, the celestite peaks intensities decreased with increasing milling

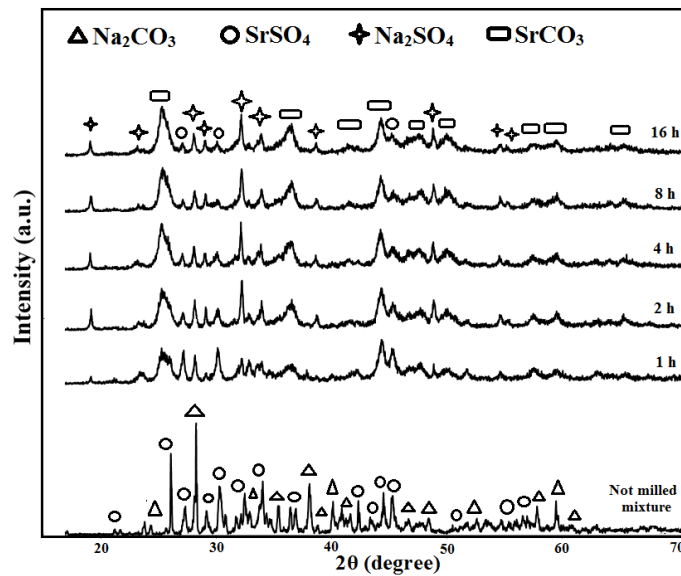


Fig. 2- XRD patterns of the milled sample for different times at constant Na₂CO₃:SrSO₄ molar ratio of 1.05:1.

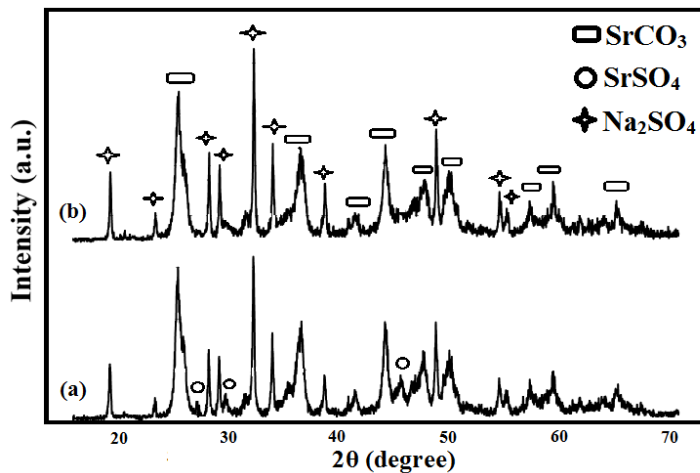


Fig. 3- XRD patterns of (a) milled sample for 16 hours in a molar ratio of 1.15:1 (b) milled sample for 2 hours in a molar ratio of 1.25:1.

time, but the peaks did not disappear completely after 16 hours. Therefore, the conversion of SrSO_4 to SrCO_3 has not been completed.

The X-ray diffraction patterns of the samples synthesized with a $\text{Na}_2\text{CO}_3:\text{SrSO}_4$ molar ratios of 1.15:1 and 1.25:1 are shown in Fig. 3. Analysis of

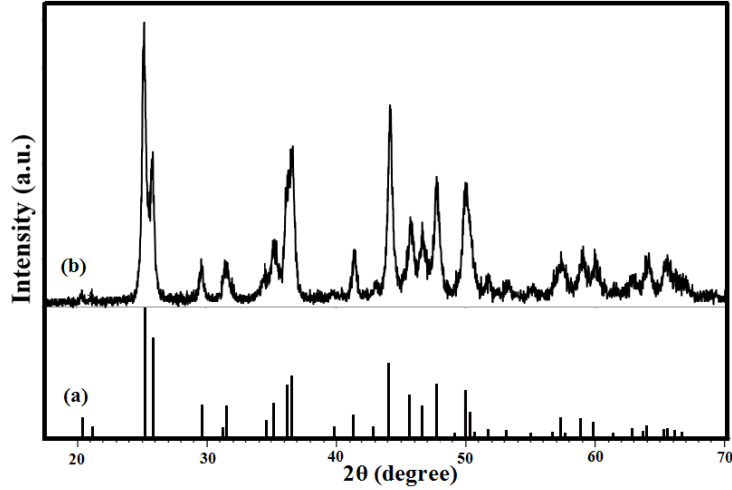


Fig. 4- (a) SrCO_3 reference pattern (JCPDS: 00-005-0418). (b) XRD pattern of 2 hours milled mixture after Na_2SO_4 removal.

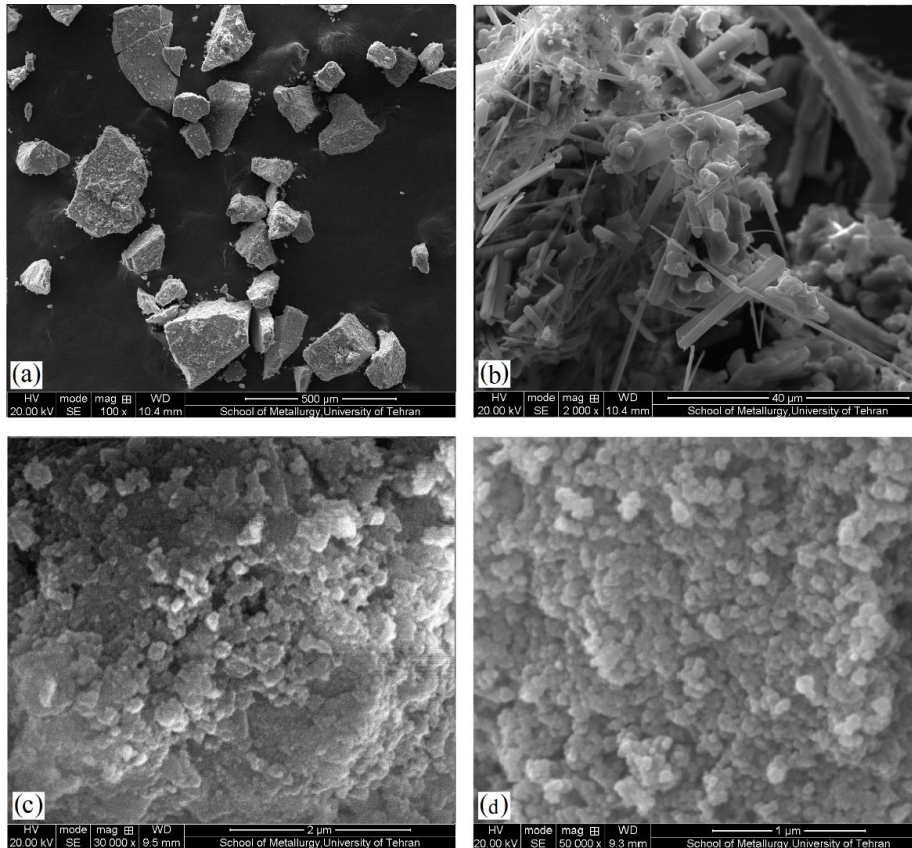


Fig. 5- The SEM micrographs: (a) celestite, (b) sodium carbonate (c) celestite and sodium carbonate mixture after 2 hours milling in 1.25:1 molar ratio, (d) Final product (SrCO_3) removed from Na_2SO_4 .

the XRD patterns revealed that increasing the ratio from 1.05:1 to 1.15:1 and 1.25:1, gave an increase in the extent of reaction. At a molar ratio of 1.15:1, the Na_2CO_3 peaks are disappeared during reaction and the celestite peaks intensities decrease on increasing the milling time but do not disappeared completely even after milling for 16 hours. It is verified that the amount of Na_2CO_3 in this molar ratio is not enough for completion of reaction. Finally, by increasing of the molar ratio to 1.25:1, the celestite peaks are disappeared completely. The excess Na_2CO_3 provides the maximum contact area between the reacting particles during milling. It is shown that the conversion has been completed in 2 hours of milling.

Fig. 4 shows the XRD pattern of milled sample for 2 hours in a molar ratio of 1.25:1 after washing by water for Na_2SO_4 removal. It is verified that Na_2SO_4 is removed from the mixture and single-phase strontium carbonate obtained. The mean crystallites size calculated by Williamson-Hall equation was approximately 32 nm.

The XRF results showed that the final product contained mainly 66.7% SrO, 1.4% CaO, 0.9% BaO and 0.5% SO_3 by weight. Since the XRF spectrometer cannot detect carbon, in accordance with XRD results which reveals the presence of SrCO_3 phase (the only Sr-containing phase), the content of SrO in XRF results is related to the SrCO_3 phase with a purity of approximately 95 wt.%. AAS results indicated that the strontium content of the feed material and the final product was 58 and 56.3%, respectively. Therefore, the recovery rate for production of SrCO_3 from celestite concentrate was about 97%.

The SEM images of processed samples are shown in Fig. 5a–d. Fig. 5a shows the celestite concentrate that contains angular particles and facet surfaces with the particle size of 100–500 μm . It should be noted that the initial powder particle size is not very critical in mechanical alloying process, except that it should be smaller than the grinding ball size. This is because the powder particle size decreases exponentially with time and reaches a small value of a few microns only after a few minutes of milling [17]. Therefore, this wide range of celestite concentrate particle size has no considerable effect on reaction progress. The needle-like particles of Na_2CO_3 are shown in Fig. 5b. As indicated in Fig. 5c, the reaction products after milling for 2 hours significantly affected by the milling and consist of spherical particles with narrow range of particle

size. It is shown in Fig. 5d that the final product (SrCO_3) contains nanoparticles with the mean size of 80 nm.

4. Conclusions

In the present investigation, mechanochemical reaction of SrSO_4 with Na_2CO_3 and preparation of nano-structured SrCO_3 has been studied as a function of the milling time and Na_2CO_3 : SrSO_4 molar ratio. The as-received celestite concentrate started to be converted into strontium carbonate in all molar ratios. In 1.05:1 and 1.15:1 molar ratios, the reaction was not completed even in extended milling time and celestite peaks remained. By increasing the molar ratio to 1.25:1, the mechanochemical reaction completed after 2 hours of milling. The Na_2SO_4 easily washed out from milled mixture by water and SrCO_3 with a purity of 95 wt.% was obtained from low-cost raw mineral celestite in an economical process. The final product consists of spherical SrCO_3 nano-particles with the mean size of 80 nm.

Acknowledgements

The financial supports of this study by the Iran Nanotechnology Initiative Council are gratefully acknowledged. Also, the support of this work by University of Tehran is thanked.

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