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Syntheses of $MgCO_3$ and $Na_2Mg(CO_3)_2$ through solid-gas reactions mediated by alkali nitrates

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ABSTRACT

In this work, we devised a set of molten salt-mediated reactions that can make use of gaseous reagents in forming solid products. In order for gaseous molecules to be reacted, its solubility in the molten salt medium needs to be high, which condition, in turn, requires the molten salt material to have a low melting point. We used alkali nitrate (ANO_3, A = Li, Na, K, Rb, and Cs) as the reaction medium, for their low melting points, for the reactions of $CO_2(g)$ with various Mg-reagents. Reactions between $4MgCO_3·Mg(OH)_2·4H_2O$ or $Mg(OH)_2$ with CO_2 in the presence of an ANO_3 above a certain quantity (30 wt% with respect to the MgO content in the Mg-reagent) produced single phase $MgCO_3$, after washing the ANO_3 with water. On the contrary, the same reactions without ANO_3 did not show any sign of incorporating gaseous CO_2 in the final products. Similarly, the reaction of a mixture between Na_2CO_3 and $4MgCO_3·Mg(OH)_2·4H_2O$ or $Mg(OH)_2$ with CO_2 in an ANO_3 medium produced $Na_2Mg(CO_3)_2$, a double carbonate of $MgCO_3$ with Na_2CO_3. The X-ray diffraction patterns and the thermogravimetry data under a CO_2 flow of $MgCO_3$ and $Na_2Mg(CO_3)_2$ indicate their high phase purity. The effects of various synthesis parameters such as the nature of ANO_3 and the amounts on the products were systematically investigated.

1. Introduction

Molten salt reactions, reactions conducted in molten salt media, have been investigated over decades. Various novel materials have been obtained by this method [1–8]. Although melting inorganic salts generally requires high temperatures, i.e., 850 °C for NaCl, they are much lower than the temperatures used in the conventional solid-state reactions. Thereby, molten salt reactions are considered to be a low temperature method. In addition, the strongly ionic nature of molten salts often renders the products novel properties. For instance, Xu et al. synthesized various metal oxide crystals with well-developed polar surfaces [9]. Solid state compounds unobtainable through the solid-state reactions can be obtained.

Molten salt reactions have been used exclusively to solid reagents. Gaseous reagents such as CO_2 to form carbonates have been excluded for this method because gas solubility in molten salts tends to decrease as the temperature increases and the temperatures for typical molten salt reactions are too high to dissolve sufficient amounts of gas. This point becomes clear by the reports of successful formation of various metal carbonates by using room temperature ionic liquids as the reaction media [10,11]. Therefore, in order to extend the molten salt reaction method to include gaseous reagents, one has to choose a salt that melts at relatively low temperatures. In order to test this idea, in this study, we investigated the formation of $MgCO_3$ and its double salt with Na_2CO_3, $Na_2Mg(CO_3)_2$, in molten alkali nitrate (ANO_3; A = Li, Na, K, Rb, and Cs) media whose melting points are known to be in the range of 255–414 °C (Melting points (°C): $LiNO_3$, 255; $NaNO_3$, 308; KNO_3, 334; $RbNO_3$, 310; $CsNO_3$, 414).

We chose to synthesize $MgCO_3$ because synthesizing crystalline anhydrous $MgCO_3$ has posed a number of challenges [12–15]. Unlike its congener $CaCO_3$ which readily crystallizes in aqueous solutions, even with the ability to differentiate one crystal structure from the others, $MgCO_3$ does not crystallize in water [14]. Any attempt to form $MgCO_3$ from aqueous solutions ended up with hydrated or basic forms of $MgCO_3$ such as $MgCO_3·xH_2O$ and $xMgCO_3·Mg(OH)_2·yH_2O$. Through reactions between Mg^{2+} and CO_3^{-} ions in formamide instead of water, Xu et al. have demonstrated that the problem lies on the unfavorable packing of carbonate ions in the crystalline $MgCO_3$ as well as on the very strong hydration of Mg^{2+} ion by water molecules [15]. Because of these problems, various synthesis methods have been put forward to synthesize anhydrous $MgCO_3$ including hydrothermal synthesis, carbonation and precipitation at elevated temperature or pressure condition.

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$Na_2Mg(CO_3)_2$ occurs naturally as a rare mineral eitelite which is a class of carbonate and nitrate according to the Nickel-Strunz mineral classification. It appears that there have been no attempt to synthesize this compound as a pure phase, although its formation has been reported when a $Mg(HCO_3)_2$ solution is flown onto a mixture of $NaHCO_3$ and Na_2CO_3 for several days [16]. Formation of $MgCO_3$ has been reported when MgO was reacted with CO_2 in the presence of an alkali nitrate [17–19]. Likewise, $Na_2Mg(CO_3)_2$ was reported to form when CO_2 was reacted with a mixture of MgO, Na_2CO_3 and $NaNO_3$ [20–23]. However, there has been no report on using molten alkali nitrate in synthesizing these compounds as pure phases.

In this work, we performed a systematic study on the molten salt synthesis of $MgCO_3$ and $Na_2Mg(CO_3)_2$ by using ANO_3 as the reaction medium, which is the first case, to our best knowledge, of extending molten salt synthesis to include a gaseous reagent. In addition, we made a few observations that seem to challenge the conventionally held views of molten salt reactions. First, we observed that the amount of molten medium could be quite small without affecting the synthesis results. Second, in some cases, ANO_3 can function as a reaction medium even when the reaction temperature is much lower than their melting points. The details are delineated in the following.

2. Experimental section

2.1. Materials

Hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$, Alfa Aesar, MgO = 40–43.5%, − 325 mesh), magnesium hydroxide ($Mg(OH)_2$, Alfa Aesar, 95–100.5%), magnesium oxide (MgO, Alfa Aesar, 99.95%), lithium carbonate (Li_2CO_3, Sigma Aldrich, 99.0%), sodium carbonate (Na_2CO_3, Sigma Aldrich, 99.5%), potassium carbonate (K_2CO_3, Sigma Aldrich, 99 +%), rubidium carbonate (Rb_2CO_3, Alfa Aesar, 99.8%), cesium carbonate (Cs_2CO_3, Alfa Aesar, 99.9%), lithium nitrate ($LiNO_3$, Sigma Aldrich, 99.0%), sodium nitrate ($NaNO_3$, Alfa Aesar, 99.0%), potassium nitrate (KNO_3, Sigma Aldrich, 99.0%), rubidium nitrate ($RbNO_3$, Alfa Aesar, 99.8%), cesium nitrate ($CsNO_3$, Alfa Aesar, 99.99%), acetone (Daejung, 99.5%), Ultrapure water (Millipore, 18.2 MΩ cm).

2.2. Synthesis of $MgCO_3$

The synthesis of anhydrous $MgCO_3$ was achieved by heating a mixture of $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ (MCH) and $NaNO_3$ (or another alkali nitrate) under a CO_2 flow, followed by washing with water. Typically, 2.338 g of MCH (equivalent to 0.025 mol of MgO (1 g) when completely converted) and a measured amount of $NaNO_3$ in a desired weight ratio (5–400 wt% and typically 30 wt% with respect to MgO) were mixed by ball milling in a 250 mL plastic bottle (Nalgene) with 50 g of acetone and 80 g of zirconia beads (Grinding Media, diameter = 10 mm) for 24 h at a speed of 60 rpm. The mixture was dried in an oven at 70 °C overnight, ground by an agate mortar and a pestle, and was placed in a tube furnace for carbonation at 325 °C for 5 h under a 100% CO_2 flow. The ramping rate of temperature was 7.5 °C/min. After the reaction, the product $MgCO_3$ was separated from $NaNO_3$ by centrifugation and washing with water for three times.

2.3. Synthesis of $Na_2Mg(CO_3)_2$

The synthesis of $Na_2Mg(CO_3)_2$ was achieved by the same process used to obtain $MgCO_3$ except that Na_2CO_3 was added in the solid mixture. Typically, 2.338 g of MCH, 3.1797 g of Na_2CO_3 (0.03 mol, 120 mol% with respect to MgO) and 1.254 g of an alkali nitrate (30 wt% with respect to MgO + Na_2CO_3) were mixed and reacted with CO_2 in the manner described in 2.2.

When necessary, especially in figures, the synthesized samples will be denoted as Product(Mg-reagent, x, alkali nitrate used) where x stands for the mass ratio of alkali nitrate with respect to the MgO (or MgO + Na_2CO_3) used as in $MgCO_3$(MCH, 4, $NaNO_3$) or $Na_2Mg(CO_3)$($Mg(OH)_2$, 0.3, $NaNO_3$).

2.4. Sample characterization

Identification of crystalline phases in the samples were achieved by powder X-ray diffraction (XRD; Rigaku D/max 2200 Ultra diffractometer; Cu Kα radiation) with a scan rate of 4 °/min. The decomposition behaviors of the $MgCO_3$ and $Na_2Mg(CO_3)_2$ products ($MgCO_3 \rightarrow MgO + CO_2$ and $Na_2Mg(CO_3)_2 \rightarrow Na_2CO_3 + MgO + CO_2$) were studied with a thermogravimetric analyzer (TGA; Hitachi Thermal Analysis, STA 7200) under a flow of 100% CO_2. The weight of the sample for each measurement was approximately 10 mg and the temperature of the TGA was increased from room temperature to 725 °C at a rate of 5 °C/min. Differential thermal analysis (DTA) was performed simultaneously. The morphology of the $MgCO_3$ or $Na_2Mg(CO_3)_2$ particles was observed by a field emission scanning electron microscope (SEM: JEOL FESEM JSM-7100F). Temperature variable in situ XRD (Rigaku SmartLab, Cu Kα, in Next-generation Catalysis Center at UNIST, Korea) was used to observe the changes of phases during the reactions. The sample temperature was varied from room temperature to 420 °C at the heating rate of 5 °C/min by using an infra-red lamp (200 V, 1800 W) and the sample was kept under a flow of CO_2 at a flow rate of 100 mL/min during the measurement. The reported temperatures of the in situ XRD data are calibrated ones by comparing the reported melting points of $NaNO_3$ and $CsNO_3$ with the temperatures at which they lose crystallinity in their in situ XRD patterns (Fig. S1). The estimated error range of the reported temperature is ± 5 °C.

3. Results and discussion

3.1. Syntheses of $MgCO_3$ in alkali nitrate media

That ANO_3 plays a key role as a reaction medium can be readily appreciated by comparing the products obtained by heating MCH in two different conditions, one with $NaNO_3$ (30 wt% to MgO in MCH) mixed with it and the other without, at 325 °C under a CO_2 flow. The XRD pattern of the product from the reaction without $NaNO_3$ (red line in Fig. 1(a)) indicates that an amorphous phase is obtained. Its TGA curve (red line in Fig. 1(b)) is almost the same as that of MCH (blue line) except that the dehydration step of MCH at < 250 °C is absent. Based on these, one can deduce that it is a dehydration product of MCH and that its composition is $4MgCO_3{\cdot}Mg(OH)_2$. The weight loss by 15.8% at 400–500 °C can be attributed to the loss of one CO_2 and one H_2O molecules, and that by 33.4% at 550–600 °C to the loss of three CO_2 molecules per formula unit. Therefore, the effect of heating MCH without $NaNO_3$ at 325 °C under a CO_2 flow is dehydration of it (Eq. (1)); reaction between CO_2 in the surrounding and the solid material does not occur. On the contrary, the product of the same reaction with $NaNO_3$ present shows a XRD pattern (black line) which can be identified as highly crystalline $MgCO_3$ without any other phase. Note that $NaNO_3$ in this sample was removed by washing with water before analyses. The phase purity of so-obtained $MgCO_3$ can be confirmed by the TGA data which shows a single weight loss step at around 630 °C (the peak position of the DTA curve) by 51.8% which is close to the theoretical value of 52.2% for the reaction $MgCO_3 \rightarrow MgO + CO_2\uparrow$. The solid product obtained after the TG measurement was identified as MgO by XRD (Fig. S2). These results clearly indicate that the presence of $NaNO_3$ leads to a reaction pathway to make use of CO_2 in the surrounding in forming the final product (Eq. (2)), which is not possible otherwise.

$$4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O \xrightarrow{CO_2, 325\ ^{\circ}C} 4MgCO_3{\cdot}Mg(OH)_2 + 4H_2O\uparrow \tag{1}$$

$$4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O + CO_2 \xrightarrow{NaNO_3, 325\ ^{\circ}C} 5MgCO_3 + 5H_2O\uparrow \tag{2}$$