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CATALYTIC EFFECT OF ALKALI CARBONATES ON THE CALCINATION OF CALCIUM CARBONATE

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ABSTRACT

Alkali carbonates (except for francium carbonate) have been tested to enhance the calcination of calcium carbonate using a Lindberg furnace and a differential thermal analysis/thermogravimetric analysis (DTA–TGA) system. The alkali carbonates were mixed with calcium carbonate (calcite) at a weight ratio of 1:20 and were studied at constant temperatures of 800 and 700 °C in a Lindberg furnace and a DTA–TGA analyzer, respectively. The results of calcination rates (wt% h^{-1}) from the Lindberg furnace and DTA–TGA analyzer have shown similarly that lithium carbonate is the best catalyst among the alkali carbonates.

INTRODUCTION

Calcination of calcium carbonate is thought to be one of the most basic and simple chemical reactions. It has been proven that the dissociation of calcium carbonate proceeds chemically by the following reaction [1]:

$$CaCO_{3(s)} \overset{\Delta}{\rightleftharpoons} CaO_{(s)} + CO_{2(g)}$$

Although the reaction is simple, commercial applications use two to four times the theoretical quantity of energy predicted from thermodynamic analysis [2].

Many researchers have attempted to reduce the energy consumption of this calcining process. Previous workers in our laboratory have tried many additives to enhance the calcination rate. They found that sodium salts of 12-molybdosilicic acid and 12-molybdphosphoric acid [2], alkali halides [3], and alkali carbonate–calcium carbonate fused salts [4] can enhance the calcination rate at constant temperatures. The common characteristic among these additives with positive catalytic effects, is that they all contain alkali metal. In order to avoid potential corrosion of alkali halides on manufacturing facilities and to prevent the tedious work for preparing fused salts, alkali carbonates have been investigated as potential catalysts for the calcination of calcium carbonate.

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EXPERIMENTAL

The alkali carbonates used in this study were lithium carbonate (MCB reagent grade), sodium carbonate (Fisher certified grade), potassium carbonate (Fisher certified grade), rubidium carbonate (Alfa reagent grade), and cesium carbonate (Alfa reagent grade). They were mixed manually to a homogeneous mixture with reagent grade calcium carbonate in a weight ratio of 1 : 20.

The samples to be run in a Lindberg furnace were weighed to 3.0000 ± 0.0020 g into casseroles. A casserole of pure calcium carbonate (as a blank) surrounded by four samples was arranged on an iron pan. Then, the pan was placed into a Lindberg furnace with the temperature setting at 800 ° C for 40 min. Subsequently, the samples were cooled in a desiccator for 40 min and weighed.

The DTA–TGA system employed in this study is a Mettler thermal analyzer with a Mettler BE 20 balance controller and a Mettler HE 20 balance. The conditions for running the DTA–TGA included a heating rate of 10 ° C min^{-1}, a chart speed of 10 cm h^{-1}, and a 2 mV range for the DTA. The reference material was alumina. The sample amount for each run was carefully controlled at 90.0 ± 0.5 mg.

Two different thermograms were obtained. One was obtained by programming the temperature to 700 ° C then keeping it constant for about 50 min. From the TGA curve the calcination rate could be calculated. The other thermogram was obtained by running the instrument to 1000 ° C. The transition temperature could then be obtained from the DTA curve.

The dissociation of calcium carbonate is independent of the geometry of the sample holder since the reaction is reversible [5]; however, the calcination rate does depend on the sample weight for each run. In order to take this factor into account, the calcination rate was expressed as:

$$\%\ \text{Calcination rate} = \frac{\text{weight loss (in mg)}}{\text{sample weight (in mg)} \times \text{time (in h)}} \times 100\%$$

RESULTS AND DISCUSSION

Table 1 summarizes the data of the calcination rate obtained from the Lindberg furnace setting at 800 ° C for 40 min. Figure 1 is the diagram plotted from the data in Table 1. Table 2 summarizes the data of calcination rate calculated from the TGA curve of DTA–TGA analyzer programmed to 700 ° C. Figure 2 is the diagram plotted from the data in Table 2. From Figs. 1 and 2, the consistency between these two different thermal methods is seen. Also, the highest catalytic effect of lithium carbonate as compared to the other alkali carbonates on calcination of calcium carbonate is observed.

TABLE 1

Calcination rate of alkali carbonates as catalysts (from Lindberg furnace at 800 ° C)

Composition (weight ratio)	Calcination rate ($wt\% \ h^{-1}$)	Av. calcination rate ($wt\% \ h^{-1}$)
1 $Li_2CO_3 + 20 \ CaCO_3$	41.72, 40.30	41.01
1 $Na_2CO_3 + 20 \ CaCO_3$	37.90, 39.64	38.77
1 $K_2CO_3 + 20 \ CaCO_3$	34.14	34.14
1 $Rb_2CO_3 + 20 \ CaCO_3$	32.97, 33.87	33.42
1 $Cs_2CO_3 + 20 \ CaCO_3$	31.62, 33.12	32.37
Pure $CaCO_3$	28.78, 28.29, 29.70 29.73, 29.01, 28.92	29.07

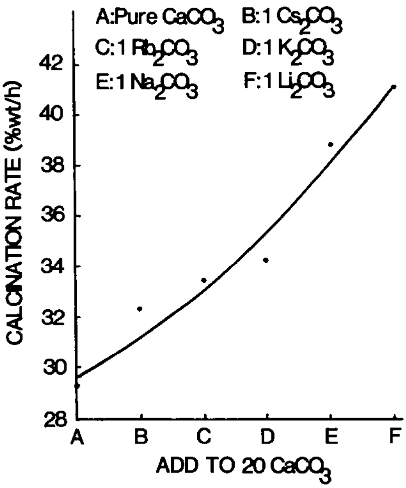

Fig. 1. Calcination rates vs. alkali carbonates (from Lindberg furnace).

TABLE 2

Calcination rate of alkali carbonate as catalyst (from DTA–TGA analyzer at 700 ° C)

Composition (weight ratio)	Calcination rate ($wt\% \ h^{-1}$)
1 $Li_2CO_3 + 20 \ CaCO_3$	33.49
1 $Na_2CO_3 + 20 \ CaCO_3$	31.60
1 $K_2CO_3 + 20 \ CaCO_3$	27.84
1 $Rb_2CO_3 + 20 \ CaCO_3$	26.74
1 $Cs_2CO_3 + 20 \ CaCO_3$.	28.66
Pure $CaCO_3$	26.39

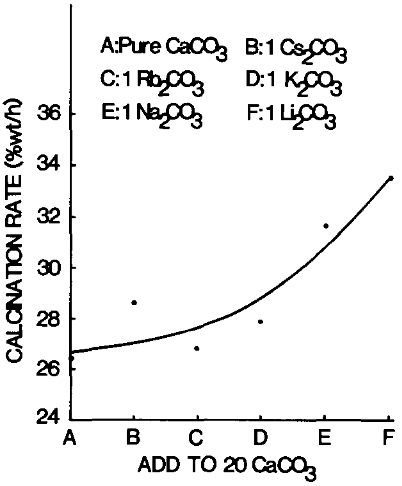

Fig. 2. Calcination rates vs. alkali carbonates (from DTA–TGA analyzer).

In the DTA–TGA thermogram, the transition temperature, the peak of the DTA curve, corresponds to the temperature of completion of calcining. Table 3 shows transition temperatures for different alkali carbonate–calcium carbonate mixtures. From Fig. 3, the alkali carbonates demonstrate a catalytic effect since calcination of calcium carbonate is completed at lower temperatures. Lithium carbonate is the best catalyst among the alkali carbonates.

The slow calcination rates of pure lithium carbonate and sodium carbonate are shown in Table 4. This explains that the enhancement of calcination by adding alkali carbonates to pure calcium carbonate is not from the calcination of alkali carbonates.

Table 5 shows the melting temperatures of alkali carbonates and calcium carbonate [6]. The melting points of alkali carbonates are relatively lower and around the dissociation temperature of calcium carbonate. The catalytic effect of alkali carbonates might be explained by a heat transfer argument [7]. When the sample particles are heated close to the melting temperature,

TABLE 3

Transition temperatures of alkali carbonate–calcium carbonate mixtures (from DTA curve)

Composition (weight ratio)	Transition temp. (°C)	Composition (weight ratio)	Transition temp. (°C)
1 $Li_2CO_3 + 20\ CaCO_3$	813	1 $Rb_2CO_3 + 20\ CaCO_3$	824
1 $Na_2CO_3 + 20\ CaCO_3$	817	1 $Cs_2CO_3 + 20\ CaCO_3$	834
1 $K_2CO_3 + 20\ CaCO_3$	822	pure $CaCO_3$	838

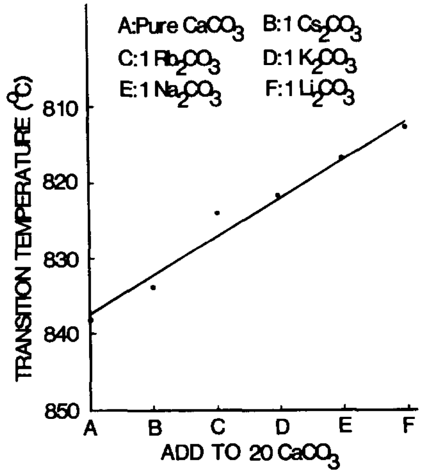

Fig. 3. Transition temperatures vs. alkali carbonate–calcium carbonate mixtures.

TABLE 4

Calcination rate of pure Li_2CO_3 and pure Na_2CO_3

Compound	Pure Li_2CO_3	Pure Na_2CO_3	
Calcination rate (wt% h^{-1})	4.99	0	13.97
Temperature (°C)	700	700	1000

TABLE 5

Melting points of alkali carbonates and calcium carbonate

Compound	Melting point (°C)	Compound	Melting point (°C)
Li_2CO_3	723	Rb_2CO_3	837
Na_2CO_3	851	Cs_2CO_3	610 (decompose)
K_2CO_3	891	$CaCO_3$	1339

they appear to contract together. This phenomenon has been proven by placing different alkali carbonates in a 700°C Lindberg furnace for 1 h. Lithium carbonate contracts to the highest degree. It pulls away from the side walls of the casserole to a larger extent than any of the other alkali carbonates. Under this circumstance, the contacting surface area of sample particles increases and, hence, the heat transfer among those particles is enhanced. As a result, the calcination rate is increased.

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