Thermochimica Acta, 118 (1987) 135–141
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

LITHIUM CARBONATE ENHANCEMENT OF THE CALCINATION OF CALCIUM CARBONATE: PROPOSED EXTENDED-SHELL MODEL

JIN-MO HUANG and KENNETH E. DAUGHERTY

Department of Chemistry, North Texas State University, Denton, TX 76203 (U.S.A.)

(Received 29 January 1987)

ABSTRACT

Lithium carbonate (Li_2CO_3) has been tested as a possible catalyst to enhance the calcination of calcium carbonate ($CaCO_3$) using a Lindberg furnace and a differential thermal analysis–thermogravimetric analysis (DTA–TGA) system. The Li_2CO_3 was mixed with $CaCO_3$ (calcite) in weight ratios ranging from 1:500 to 1:20 and the mixtures were studied at constant temperatures of 800 and 700 °C in a Lindberg furnace and using a DTA–TGA analyzer. The results of the calcination rates (wt.% h^{-1}) both from the Lindberg furnace and from the DTA–TGA analyzer have shown that the Li_2CO_3–$CaCO_3$ mixture of about 1:200 has the highest calcination rate. In order to explain the data, a physical model is proposed. This extended-shell model has been tested with 5% magnesium chloride–calcium carbonate ($MgCl_2$–$CaCO_3$) and 5% calcium chloride–calcium carbonate ($CaCl_2$–$CaCO_3$) samples.

INTRODUCTION

In the previous paper [1], lithium carbonate (Li_2CO_3) was proved to be the best catalyst among alkali carbonates for the calcination reaction:

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g)$$

The increase in the calcination rate is due to the enhancement of heat transfer on the addition of alkali carbonates to calcium carbonate ($CaCO_3$).

It is apparent that the calcination reaction starts at the outside surface and proceeds towards the center of the sample. Furnas [2] and others have suggested the shell model (Fig. 1) for the decomposition of $CaCO_3$. In this model, heat transfer and mass transfer (the removal of CO_2) play the important roles. According to Satterfield and Feakes [3], the calcination rate is determined by the interrelationships between three major rate processes. *(1) Heat transfer.* It is clear that heat must be transferred from the surface to the center of the sample. If the heat-transfer process can be enhanced, the calcination rate will be increased.

0040-6031/87/$03.50

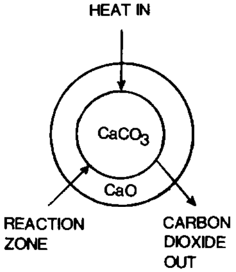

Fig. 1. Decomposition of a sphere of $CaCO_3$ (shell model).

(2) Mass transfer. The CO_2 released from the reaction must escape through the outer shell of calcium oxide (CaO). The increase in CO_2 pressure requires an increase in the temperature of the reaction zone to maintain decomposition. Also, according to Le Chatelier's principle, the quick removal of CO_2 will promote the reaction to the right.

(3) Chemical reaction. From the kinetic point of view, the activation energy might be the rate-limiting factor. If the activation energy of a reaction can be reduced, the reaction rate will be increased.

The purpose of the present study was to determine the relation of the Li_2CO_3 concentration and its catalytic effect on the calcination of $CaCO_3$. Furthermore, a physical model was developed in order to explain the catalytic phenomenon found in this study.

EXPERIMENTAL

Lithium carbonate (MCB reagent grade) was mixed manually to a homogeneous mixture with $CaCO_3$ (reagent grade) in weight ratios ranging from 1 : 500 to 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 $CaCO_3$ (as blank) surrounded by four samples was arranged on an iron pan. Then the pan was placed into a Lindberg furnace with a temperature setting at 800 °C for 40 min. After that the samples were cooled in a desiccator for 40 min and weighed.

The DTA–TGA system 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 programmed to a temperature of 700 °C, and then kept constant for about 50 min. From the TGA curve the calcination rate was calculated. The other thermogram was obtained by running the instrument to 1000 °C, and the transition temperature was obtained from the DTA curve.

The dissociation of $CaCO_3$ is independent of the geometry of the sample holder since the reaction is reversible [4], but 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

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

RESULTS AND DISCUSSION

Table 1 summarizes the data on the calcination rate obtained from the Lindberg furnace setting at 800 °C for 40 min. Figure 2 is the diagram plotted from the data in Table 1. Table 2 summarizes the data on the calcination rate calculated from the TGA curve of the DTA–TGA analyzer programmed to 700 °C. Figure 3 is the diagram plotted from the data in Table 2. From Figs. 2 and 3, the consistency between these two different methods is seen. Also, the greatest catalytic effect of 0.4%–0.6% Li_2CO_3 in $CaCO_3$ as compared with the other concentrations of Li_2CO_3 in $CaCO_3$ on the calcination of $CaCO_3$ is observed.

In the DTA–TGA thermogram, the transition temperature, the peak of the DTA curve, corresponds to the temperature at the completion of calcination. Table 3 shows transition temperatures for different compositions of Li_2CO_3–$CaCO_3$ mixtures. In Fig. 4, the catalytic effect of Li_2CO_3 is demonstrated by the completion of the calcination of $CaCO_3$ at lower temperatures. Furthermore, Li_2CO_3 enhances the calcination rate by ap-

TABLE 1

Calcination rate with Li_2CO_3 as catalyst (from Lindberg furnace at 800 °C)

Wt.% of Li_2CO_3 added to 100% $CaCO_3$	Calcination rate (wt.% h^{-1})	Av. calcination rate (wt.% h^{-1})
0.2	42.36, 42.48	42.42
0.3	44.24, 44.10	44.17
0.4	45.62, 44.25	44.94
0.6	44.79, 43.74	44.26
0.8	45.36, 44.24	44.80
1.0	43.46, 43.83	43.64
2.0	41.86	41.86
5.0	41.72, 40.30	41.01
Pure $CaCO_3$	28.78, 28.29, 29.70, 29.73, 29.01, 28.92	29.07

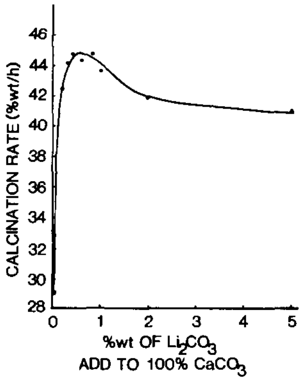

Fig. 2. Calcination rate vs. concentration of Li_2CO_3 (from Lindberg furnace).

TABLE 2

Calcination rate with Li_2CO_3 as catalyst (from DTA–TGA analyzer at 700 ° C)

Wt.% of Li_2CO_3 added to 100% $CaCO_3$	Calcination rate (wt.% h^{-1})
0.2	34.57
0.3	36.95
0.4	39.67
0.6	39.90
0.8	37.42
1.0	32.89
2.0	34.30
5.0	33.49
Pure $CaCO_3$	26.39

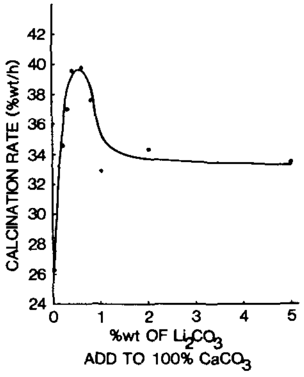

Fig. 3. Calcination rate vs. concentration of Li_2CO_3 (from DTA–TGA analysis).

TABLE 3

Transition temperature of Li_2CO_3–$CaCO_3$ mixtures (from DTA curve)

Wt.% of Li_2CO_3 added to 100% $CaCO_3$	Transition temperature (°C)
0.1	815
0.2	780
0.4	773
0.6	788
1.0	793
2.0	795
5.0	813
Pure $CaCO_3$	838

proximately 50% at the low concentration of 0.4 wt.% in $CaCO_3$. Thus, the potential contamination of lime with lithium metal can be minimized in a commercial operation.

In the work of Satterfield and Feakes [3], it was found that the temperature at the center of the sample rose rapidly to a maximum, and then, after a small temperature drop, passed through a minimum. The temperature remained practically constant for the major part of the reaction time and it also remained substantially in excess of the equilibrium temperature throughout the run. This suggests that after the decomposition of the outer layer of the sample, the formation of CaO does hinder heat transfer in the calcination process. This is because the thermal conductivity and the bulk density [3] of CaO are relatively lower than those of $CaCO_3$. The low thermal conductivity of CaO hinders the heat transfer from the outer to the inner portion of the sample. While the low bulk density of CaO means that there is more void space among sample particles, the conduction of heat decreases. Also, Haslam and Smith [5] treated the decomposition of $CaCO_3$

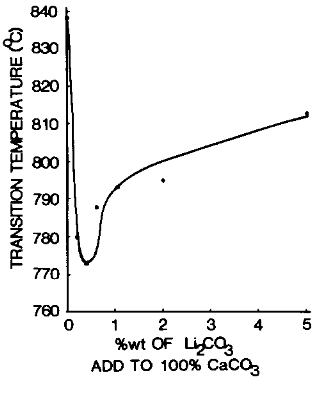

Fig. 4. Transition temperature vs. Li_2CO_3 concentration.

TABLE 4

Calcination rate of $CaCO_3$ at different temperatures

Temperature (°C)	Calcination rate (wt.% h^{-1})
700	26.39
800	168.19

as a process involving only heat transfer. It is clear that heat transfer is a very important factor.

Wist [6] pointed out that the calcination rate of $CaCO_3$ is directly proportional to the difference between the CO_2 pressure inside and outside the reaction zone. Therefore, mass transfer has an important role as well.

The data reported for the activation energy of this reaction are between 35.5 and 50.1 kcal mol^{-1} [7–10]. The calcination rates from TGA curves at different temperatures (Table 4) tell us that chemical reaction is not, relatively, an important factor from 700 to 800 °C, because the calcination rate increases only about sixfold (theoretically the rate might increase 1024-fold). This means that the other factors, heat transfer and mass transfer, govern the calcination rate more than do the kinetics.

From the above discussion and the results of previous work in this laboratory [1], an extended-shell model (Fig. 5), which can explain the data from this work by using the heat transfer and mass transfer argument, has been developed. When Li_2CO_3 is added to $CaCO_3$ and the mixture is heated to the temperature (700 °C) of calcination, the particles of Li_2CO_3 begin to contract. This contraction increases the contacting surface area among the sample particles. Hence, heat transfer is enhanced and the calcination rate increases. When the amount of Li_2CO_3 in the mixture is greater than 0.8%, the contraction is so great that the interstitial space among sample particles is small. This situation prevents the CO_2 from escaping freely. Thus, the pressure of CO_2 is increased. As a result, the calcination rate decreases. This is why the relationship between calcination rate and concentration of Li_2CO_3 is mountain shaped.

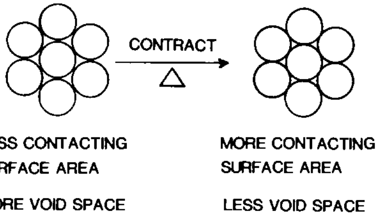

Fig. 5. The extended-shell model.

TABLE 5

Melting temperature of $MgCl_2$ and $CaCl_2$

Compound	Melting temperature (°C)
$MgCl_2$	714
$CaCl_2$	782

TABLE 6

Calcination rates of $CaCO_3$ with 5% $MgCl_2$ and 5% $CaCl_2$ in $CaCO_3$ (from DTA–TGA analyzer at 700°C)

Mixture	Calcination rate (wt.% h^{-1})
5% $MgCl_2$ + 100% $CaCO_3$	37.19
5% $CaCl_2$ + 100% $CaCO_3$	34.03
Pure $CaCO_3$	26.39

In order to predict other possible catalysts for calcination by using this extended-shell model, magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$), both having melting temperatures (Table 5) [11] close to the calcination of $CaCO_3$ and contracting at a temperature of 700°C, were chosen. The calcination rates of 5% $MgCl_2$ and 5% $CaCl_2$ in $CaCO_3$ are shown in Table 6. Because $MgCl_2$ contracted more than $CaCl_2$ after being placed in a Lindberg furnace at 700°C for 60 min, $MgCl_2$ enhanced the calcination rate more than $CaCl_2$. Other possible catalysts may be chosen to refine further this proposed extended-shell model.

REFERENCES

1 J.M. Huang and K.E. Daugherty, Catalytic effect of alkali carbonates on the calcination of calcium carbonate, Thermochim. Acta, accepted for publication.
2 C.C. Furnas, Ind. Eng. Chem., 23 (1931) 534.
3 C.N. Satterfield and F. Feakes, AIChE J., 5 (1959) 115.
4 W.W. Wendlandt, Thermal Methods of Analysis, 2nd edn., Wiley-Interscience, New York, 1974, Chapter 1.
5 R.T. Haslam and V.C. Smith, Ind. Eng. Chem., 20 (1928) 170.
6 A.O. Wist, Therm. Anal. Proc. Int. Conf., 2nd 1968 (published 1969), Vol. 2, p. 1095.
7 H.T.S. Britton, S.J. Gregg and G.W. Winsor, Trans. Faraday Soc., 48 (1952) 63.
8 H. Kappel and G.F. Huttig, Kolloid-Z., 91 (1940) 117.
9 C. Slonim, Z. Elektrochem., 36 (1930) 439.
10 J. Splichal, St. Skramovoky and J. Goll, Collect. Czech. Chem. Commun., 9 (1937) 302.
11 R.C. Weast, Handbook of Chemistry and Physics, 60th edn., Chemical Rubber Company, Boca Raton, FL, 1980.