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Effect of LiCl on the Rate of Calcite Decomposition

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ABSTRACT

The rate of decomposition of calcite powder in vacuum has been measured by the Langmuir and Knudsen methods. Measured pressures in effusion cells in the absence of additives approach the equilibrium value. The Langmuir experiments gave an apparent equilibrium CO_2 pressure $\sim 3 \times 10^{-4}$ times the known pressure for the reaction. It is suggested that the CO_2 is in equilibrium with the calcite, but the CaO is not. In Langmuir experiments 10 wt.% LiCl does not increase the initial decomposition rate. In the Knudsen cells, 10 wt.% LiCl can increase the initial rate by $>2\times$. LiCl reduces the surface area of the product CaO under either condition from $>30 \text{ m}^2/\text{g}$ to $\sim 1 \text{ m}^2/\text{g}$. Probably a LiCl-CaO eutectic provides a solution path for CaO recrystallization and, at high CO_2 pressures, also for CaCO_3 decomposition.

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I. INTRODUCTION

Three carbonate decomposition reactions studied in our laboratory¹⁻⁴ proceed at rates only 10^{-4} to 10^{-5} times rates that are theoretically possible. If effective decomposition catalysts can be found, such commercially important materials as CaO and MgO might be produced by decomposing carbonates at considerably lower temperatures than presently required, with significant savings in energy.

Hildenbrand and co-workers recently succeeded in catalyzing MgSO_4 decomposition. They attributed the enhanced decomposition rate when Pt or Fe_2O_3 were present to increased rates of conversion of $\text{SO}_3(\text{g})$ to $\text{SO}_2(\text{g})$ plus O_2 .^{5,6} Rates of vaporization of elemental arsenic⁷ and of decomposition of solid GaN ⁸ are increased by liquids in which the vaporizing phases are partially soluble. No one has attempted to catalyze a carbonate decomposition. It seemed of interest to explore the possibility that calcite decomposition could be catalyzed by additions of salts which might dissolve some of the carbonate phase.

Rates of decomposition, with and without possible catalysts, were measured in vacuum for calcite powder in open crucibles (the Langmuir method) and in crucibles with small orifices (the Knudsen effusion method). Knudsen effusion studies had not previously been reported for calcite. Effusion studies for $\text{Mg}(\text{OH})_2$ ⁹ and dolomite⁴ [$\text{MgCa}(\text{CO}_3)_2$] decomposition yield apparent equilibrium pressures several orders of magnitude lower than the true values. The reason for these inconsistencies is not understood. It was of interest to determine

whether effusion measurements with calcite also yield low apparent equilibrium pressures.

It was also of interest to determine whether liquid-phase additives might significantly change the surface area and morphology of the CaO produced by calcite decomposition in vacuum. In the absence of additives, these particles are only ~10 nm cross-section.^{1,10-13} Such small particles might be highly reactive toward solution in molten salts as they are with water vapor.^{10,11}

Decomposition rates in effusion cells with 1 mm diameter orifices were measured for calcite alone and with each of several possible catalysts present. The effects of LiCl on decomposition rates and on the morphology and surface area of the CaO product were examined for a broader range of conditions.

II. EXPERIMENTAL

For the Langmuir measurements, a Pt basket was hung from a recording microbalance in a Pt resistance furnace. The pressure was maintained $<1.3 \times 10^{-4}$ Pa. For effusion measurements, graphite cells with tight-fitting lids having orifice diameters of 1.0 mm and 0.23 mm were used. The samples were held for at least 30 minutes at each temperature to insure that equilibrium was achieved.

The temperature was measured with a Pt-Pt/10% Rh thermocouple, and was controlled to $\pm 2^\circ\text{C}$. Sample weight losses were continuously measured on a strip chart recorder with a sensitivity of either 100 mg or 10 mg full scale.

The sample temperature was calibrated by determining the vapor pressure of NaCl in the temperature range of interest in effusion cells using the Knudsen effusion technique. Measured pressures were within 3 percent of the accepted values.

Low alkali reagent grade CaCO_3 , of 2 to 5 μm average particle size, was used for all experiments. The surface area of the powder was found by the BET method to be $\sim 0.6 \text{ m}^2/\text{g}$. For catalytic experiments, reagent grade LiCl, NaCl, Fe_2O_3 , and Na_2CO_3 powders were intimately mixed with the CaCO_3 . These substances all have vapor pressures which are lower than the equilibrium decomposition pressure of calcite. The manufacturer's analysis of the CaCO_3 and spectrographic analysis of the LiCl are given in Table I.

For XRD measurements, powder samples were packed in an Al holder and irradiated with $\text{CuK}\alpha$ radiation. The XRD samples were analyzed directly after removal from the thermobalance to minimize hydration of the CaO.

Samples of CaO for SEM study were dispersed in CCl_4 upon removal from the furnace to avoid hydration and agglomeration. The CaO dispersion was dropped upon a holder using an eyedropper, and a layer of Au approximately 20 nm thick was deposited on the powder.

III. RESULTS AND DISCUSSION

Extrapolations to zero orifice diameters of pressures measured in effusion cells with different orifice diameters (the Whitman-Motzfeld

extrapolation)^{14,15} are expected to give the equilibrium pressure for the reaction.¹⁶ The method works satisfactorily for MgSO_4 decomposition, for example, provided the complexity of the vapor is taken into account.^{5,6} However, decomposition pressures calculated for dolomite and $\text{Mg}(\text{OH})_2$ by this method are several orders of magnitude lower than the well-established equilibrium values.^{9,10} The reason for these large discrepancies is not known.

In the present study, initial pressures were calculated from the mass fluxes by means of the Hertz-Knudsen-Langmuir equation.¹⁶ At 600 to 700°C these values were ~10 to 20% of the equilibrium values for the cell with the 1 mm diameter orifice. For the cell with the 0.23 mm orifice, pressures were ~40 to 60% of the equilibrium value (Fig. 1). Because the measured fluxes are high enough to make the mean-free path of molecules in the vapor short relative to the diameter of the effusion orifice, pressures calculated by means of the Hertz-Knudsen-Langmuir equation may be higher than the true pressures by a factor between 1 and 1.7.¹⁷ Within this level of uncertainty it is clear that calcite decomposition differs from decomposition of dolomite or $\text{Mg}(\text{OH})_2$ in that calcite decomposition pressures approach their equilibrium values in effusion cells with relatively small orifices.

In contrast, initial CO_2 fluxes measured at 600°C for Langmuir samples that weighed 0.1, 0.5, and 1.0 g were 2.5×10^{-7} , 4.6×10^{-7} , and 3.3×10^{-7} moles/sec-cm² of bed cross sections. These fluxes average only about 3×10^{-4} times the fluxes that would be measured if

the true equilibrium decomposition pressure¹⁸ were developed in the bed. For a reaction so far from equilibrium, the CO_2 flux per unit area of bed cross section would be expected to vary in direct proportion to the quantity of sample—that is, by a factor of 10 when the weight of CaCO_3 was increased from 0.1 to 1.0 g. Instead, the initial flux remains $\sim 3 \times 10^{-7}$ moles/sec-cm² independent of sample weight. This behavior implies that a low metastable equilibrium pressure has been established in the powder bed.

In principle, low equilibrium decomposition pressures could result for CaCO_3 decomposition if the solid decomposition product is unstable by $-RT \ln 3 \times 10^{-4} \approx 67,000$ joules. (This unlikely possibility will be tested by measuring thermodynamic properties of the product solid.) It seems more probable, however, that during decomposition in vacuum, calcite, and $\text{Mg}(\text{OH})_2$ and dolomite as well, are close to equilibrium with their gaseous decomposition products, but are not at equilibrium with their solid products. XRD studies of carbonate decomposition reactions suggest that the gaseous product diffuses from small volume elements of the reactant, and the solid product phase then forms by a cooperative process such as twinning^{19,20} or shear. A cooperative process is not inherently reversible as is diffusion.²¹

The kind of metastable equilibrium behavior observed for $\text{Mg}(\text{OH})_2$, dolomite, and calcite may prove to be common for decomposition reactions in which the solid product is formed at only a small fraction of the temperatures required to provide ready condensed-phase diffusion.

For most such decomposition reactions in vacuum, the solid product probably forms by a nondiffusional process.

The initial rate at which calcite decomposed in the effusion cells with 1 mm diameter orifices was little affected by the presence of 10 wt.% of Fe_2O_3 or of Na_2CO_3 . Additions of 10 wt.% NaCl or LiCl , on the other hand, increased the initial rates of weight loss. LiCl appeared to have the larger effect, and its influence on decomposition rates was studied further. In Fig. 2 the measured temperature dependencies in the two effusion cells are compared to the equilibrium pressure calculated from thermochemical data. The rates measured in the cell with the 1 mm orifice are ~2 times initial rates measured in the absence of a catalyst in the same cell. The rates measured in the cell with the 0.23 mm orifice are ~2.5 times the initial uncatalyzed rates (Fig. 3).

When calcite was heated without LiCl , rates of weight loss decreased from the beginning of each run. When LiCl was mixed intimately with the calcite, the weight-loss rates in both cells remained constant until ~90% of the calculated CO_2 content of the calcite had escaped. The rate then decreased markedly to the rate calculated from the vapor pressure of LiCl .

Thermodynamic calculations indicate that no significant concentration of vapor molecules should result from the CaCO_3 and LiCl mixture other than CO_2 , LiCl , and Li_2Cl_2 . Vaporization of LiCl and Li_2Cl_2 at the maximum rate possible^{1,16} for pure LiCl could account

for $\sim 1/2$ the increase in flux from the cell with a 1.00 mm orifice. However, the maximum contribution of LiCl and Li_2Cl_2 to the flux from the cell with the 0.23 mm orifice is $\sim 8\%$. Evidently, the LiCl provides a path for CaCO_3 decomposition that increases the decomposition rate by >2 times at 700°C .

The effectiveness of a catalyst is usually greatest when a reaction is far from equilibrium because, as equilibrium is approached, the catalyst increases the rate of the reverse reaction as well as of the forward reaction. However, mixtures of ~ 10 wt.% LiCl with calcite in a Langmuir cell, where CO_2 pressures are $<10^{-2}$ times those in the Knudsen cell, causes no increase in initial weight losses (Fig. 4). If there were no LiCl- CaCO_3 interaction, the LiCl weight loss alone should be higher than the weight loss measured in the Langmuir cell; the catalysis of calcite decomposition by LiCl does not occur at low CO_2 pressures at 600°C .

Figure 5 shows the morphology of CaO formed in either the Langmuir or effusion cell runs when no additive is present. Surface areas of $\sim 90 \text{ m}^2/\text{g}$ are found for the CaO produced in the Langmuir runs or in the effusion cell with the 1 mm diameter orifices. CaO from the cell with the 0.23 mm orifice had a surface area of $\sim 30 \text{ m}^2/\text{g}$. XRD peaks for these samples are broad. All these observations are consistent with results of a more detailed investigation of the influence of CO_2 pressure on the CaO produced by calcite decomposition.¹¹

The internal porosities of the particles seen by SEM are known to be of the order of 50%,¹³ but the pores are too small to resolve with the SEM. Figure 6 shows the very different morphology of the low surface area CaO produced when decomposition occurred in the presence of LiCl, and when heating was continued to vaporize all LiCl from the samples. The surface area of this material is $\sim 1 \text{ m}^2/\text{g}$, so low that internal porosity must be negligible. The XRD patterns are characteristic of a well-crystallized CaO.

The increase in crystallinity and reduction in surface area of CaO produced from calcite decomposition in the presence of LiCl is probably a consequence of solution of small particles of CaO in a melt of LiCl and CaO with the subsequent growth of large CaO particles from the melt. The melting point of LiCl is 614°C ²²; the solubilities of CaO and CaCO_3 in liquid LiCl are not known. The catalytic effect of LiCl at high CO_2 pressures probably reflects solution of calcite in the melt followed by its decomposition there.

It is surprising that LiCl causes such a dramatic change in the morphology and crystallinity of CaO at temperatures as low as $600\text{--}700^\circ\text{C}$. To determine whether calcite or CO_2 is necessary to the recrystallization process, a sample of CaO of $90 \text{ m}^2/\text{g}$ surface area was heated in vacuum in the presence of 10 wt.% LiCl for a period comparable with that required to decompose a calcite sample. SEM photographs of the product CaO after elimination of the LiCl by continued heating (Fig. 7) show particles which have shapes like those of the original high-surface

area CaO, but the linear dimensions of the particles have decreased to 2 μm or less from initial dimensions of the original particles of 5 μm or more. Furthermore, some areas of the micrographs show rounded surfaces, which suggests that the original block-like aggregates of very small CaO crystals have partially dissolved and reprecipitated. The small block-like volume elements may still be porous, but access to any pores has been closed, presumably by recrystallized CaO. The surface area of this material was only $\sim 1 \text{ m}^2/\text{g}$.

CONCLUSIONS

When calcite powder is decomposed in Knudsen cells at 600°C to 700°C, measured decomposition pressures approach their equilibrium values. In cells without lids, measured fluxes per cross section of bed at 600°C are only $\sim 3 \times 10^{-4}$ times those which correspond to the equilibrium decomposition pressure. The observation that this flux is not increased when sample weight is increased from 0.1 g to 1 g indicates that a highly metastable equilibrium is established.

When calcite powder is decomposed alone in vacuum, CaO is formed as a poorly crystalline porous powder CaO of high surface areas, $\sim 90 \text{ m}^2/\text{g}$ at 700°C. If $\sim 10 \text{ wt.}\%$ LiCl is mixed with calcite and then evaporated from the sample after decomposition is complete, the CaO is produced in a well-crystallized form of surface area $< 1 \text{ m}^2/\text{g}$. LiCl also reduces the surface area of CaO that was initially formed in the absence of LiCl. Probably the high surface area CaO dissolves in liquid LiCl and recrystallizes from the melt.

At CO_2 pressures only a little below the equilibrium decomposition pressure at 700°C , liquid LiCl increases the rate of calcite decomposition by $>2x$. High CO_2 pressures probably increase the solubility of calcite in the melt or the rate at which calcite dissolves in it, and the increased decomposition rate is a consequence of the liquid phase path.

For commercial applications, a much more effective catalyst would be required. The increase in decomposition rate produced by LiCl would not justify the expense of mixing calcite with LiCl and recovering it after calcite decomposition is complete.

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Table 1

Calcium carbonate

Cl	0.001
F	0.001
SO ₄	0.005
Ba	0.002
Heavy metals	0.005
Fe	<0.0005
Mg	<0.01
K	0.008
Na	0.007
Sr	0.01

Lithium chloride

Ca	0.01
ClO ₃	0.001
Heavy metals	0.002
Fe	0.001
NO ₃	0.001
K	0.01
Na	0.20
SO ₄	0.01

Figure Captions

- Fig. 1. Uncatalyzed initial decomposition pressures of calcite. Open circles, 0.23 mm orifice. Closed circles, 1.00 mm orifice. Solid line indicates pressures calculated from thermochemical data.
- Fig. 2. Decomposition pressures for calcite in the presence of 10 wt.% LiCl. Open squares, 0.23 mm orifice. Closed squares, 1 mm orifice. Solid line indicates pressures calculated from thermochemical data.
- Fig. 3. Weight losses as a function of time in cell with 0.23 mm orifice. Lower curve, calcite only. Upper curve, with 10 wt.% LiCl.
- Fig. 4. Weight losses as a function of time from calcite in an open-topped basket. Lower curve, calcite only. Upper curve, with 10 wt.% LiCl.
- Fig. 5. CaO porous powder particles formed by decomposition of calcite in vacuum.
- Fig. 6. CaO particles formed by decomposing calcite in vacuum with 10 wt.% LiCl present.
- Fig. 7. CaO formed from heating the porous CaO powder of Fig. 5 in vacuum with 10% LiCl. Note decrease in particle exterior dimensions.

XBL8II-5103A

Figure 1

XBL 811-5105A

Figure 2

XBL 81I-5104

Figure 3

Figure 4

XBL804-4996

XBB 784-4505

Figure 5

5 μm

XBB 790-12872

Figure 6

XBB 790-15766

Figure 7