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DISCLAIMER

KINETICS OF TRANSPORT OF CO_2 THROUGH POROUS CaO AND BaO FORMED BY CARBONATE DECOMPOSITION

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The decomposition of single crystals of five complex salts, among them $CaCO_3$[1] and $BaCO_3$[2], has been studied in our laboratory under conditions that should make the rate limiting process either a chemical step or the escape of the gaseous reaction product through the porous solid product. Rates of these decomposition reactions were not measurably affected by the formation of solid product layers that approached 1 mm in thickness.

Measurable effects might be expected. Gas phase transport through porous solids under the conditions of these studies is by Knudsen flow. Knudsen flow through a porous barrier reduces the flux density of gases from equilibrium sources by a transmission factor $C = fc/(\ell+fc)$, where ℓ is the barrier thickness, f is the porosity and c is a constant of the order of the average pore diameter.[3,4] For CaO produced by decomposition of calcite ($CaCO_3$) single crystals, $f = 0.54$ and pore diameters are presumed to be less than 0.05μm because the pores could not be observed in scanning electron microscope (SEM) pictures. Thus the value of C would be expected to vary from 1 to less than 10^{-4} as the CaO layer on calcite grew[2] to about 1 mm thickness.

C is essentially the probability that a gas molecule which enters a porous barrier will escape at the other side without being returned at least once to the entrance side. A general theory for decomposition reactions[4] predicts that the decomposition rate can remain independent of the thickness of a porous product layer only so long as $C \cong fc/\ell$ is larger than J_i/J_{eq}, where J_i is the decomposition flux density measured in vacuum for a negligible product layer thickness and J_{eq} is the flux density calculated from the equilibrium decomposition pressure by means of the Hertz-Knudsen-Langmuir equation. Values of J_i/J_{eq} are often known, but experimental values of C, which can be used to test the theory have not been available.

This note reports values of C and the derived constant c for the porous oxides produced by complete decomposition of single crystals of witherite ($BaCO_3$) and of calcite. Besides being used to test the theory, values of c are compared with average diameters of pores which are estimated for the oxides from SEM observations and from BET surface area measurements.

Single crystals of each carbonate were split into wafers along natural cleavage planes and were cut to 0.7 cm diameter disks. The disks were mounted between an alumina collar and a smooth-ground alumina tube in a Nuclide mass spectrometer. Leakage of He gas around the disk edges was measured at room temperature from the rate of pressure drop in an inlet system of known volume. Pressures of 1 to 100μm were used. Each disk was decomposed in situ to the oxide, and the pressure drops of He and CO_2 through the disks were measured at high temperature and, for the BaO disks, again at room temperature with He.

The calcite disks were, with one exception, 0.4 to 0.5 mm thick. The witherite and remaining calcite disks were about 1 mm thick. To correct for gas leakage around the disk edges, apparent transmission factors measured for the non-porous carbonate disks were subtracted from apparent factors measured after decomposition to obtain transmission factors reported in column 4 of Table I. Because the most probable source of serious error is the development of cracks or of increased leakage at the disk edges during decomposition of the carbonates, the smaller transmission factors measured for each oxide probably are the better values. A more conservative view is that because of the possibility of increased leakage after decomposition is complete, all the measured transmission factors should be considered to be upper limits.

For transport by Knudsen flow, values of c are expected to be close to the average pore dismeter.[3,4] Values measured with CO_2 and He for BaO range from 1 to 5μm. Average pore diameters of 3.5 and 11μm are estimated for two BaO samples from BET measurements of the surface area, assuming tubular pores. Diameters observed in SEM photographs range from 2 to 10μm.

For CaO the data yield $c \leqq 0.5$μm. Our SEM examination failed to resolve pores (which implies pore dimensions less than 0.05μm) but reveals a ridged fracture pattern, with about 2μm spacing between ridges. If the high surface area found by the BET method, $100\mu m^2/g$, is assumed to reflect tubular pores, an average pore diameter of 7×10^{-3}μm is calculated.

The transmission properties of the BaO are nicely accounted for by Knudsen flow. For CaO the data for both pore dimensions and gas transmission are inconclusive.

The high surface area of CaO may arise from a structure in which one set of pores has dimensions of the order of 7×10^{-3}μm or smaller, and a second set has dimensions of the order of 2μm, as suggested by the ridge structure. Observation of the CaO formed by direct decomposition in an electron microscope should settle this question.

The true value of c for the CaO may lie anywhere in the range from $2 \times 10^{-3}\mu m$ to $0.5\mu m$. The lower values would be consistent with a structure in which all pores cluster in dimensions near the value suggested by the surface area measurements. The higher values could arise either because some pores are of the order of $1\mu m$ dimensions or because surface diffusion is important.

These uncertainties carry over to a test of the theory. For CaO, $J_i/J_{eq} = 10^{-5}$[5] compared to $10^{-6}<c<3 \times 10^4$ when $\ell \cong 1$ mm from alternate interpretations of the barrier measurements. For BaO, the barrier properties are consistent with expectations from the theory. For $\ell = 1$ mm, $C \cong 2 \times 10^{-3}$ compared to $J_i/J_{eq} = 2 \times 10^{-4}$.

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5. This is a corrected value. In reference 1, J_{eq} was miscalculated and J_i/J_{eq} was incorrectly reported to be 10^{-3}.

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Table I. Transmission Data for Porous CaO and BaO

Oxide	Temp °K	Gas	Leak Constant ($\times 10^4$)	Transmission factor($\times 10^4$)	Equivalent diameter c (μm)
CaO	1028	He	2.2	3.5	.35
CaO	1031	CO_2	2.2	1.8	.19
CaO	884	He	1.4	4.0	.35
CaO	884	CO_2	1.4	3.3	.29
CaO	953	He	8.0	14	1.5
CaO	953	CO_2	8.0	8.0	.86
CaO	974	He	1.2	3.2	.33
CaO	973	CO_2	1.2	2.6	.27
CaO	1022	He	8.5	12	2.4
CaO	1022	CO_2	8.5	11	2.2
BaO	1300	He	4.9	8.5	1.7
BaO	1300	CO_2	4.9	7.0	1.4
BaO	295	He	4.9	14	2.8
BaO	1316	He	12	9.0	2.9
BaO	1316	CO_2	12	7.5	2.4
BaO	299	He	12	11	3.6
BaO	1294	He	5.5	11	2.6
BaO	1294	CO_2	5.5	17	3.8
BaO	295	He	5.5	22	4.9
BaO	1332	He	8.5	5.5	1.2
BaO	1332	CO_2	8.5	11	2.4
BaO	310	He	8.5	8.0	1.8

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