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ACTIVE OXIDES

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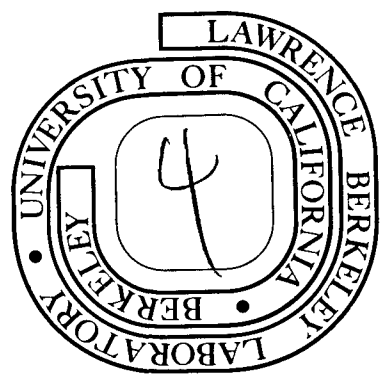
Alan W. Searcy

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RESEARCH HIGHLIGHT

ACTIVE OXIDES

Solid oxides are important in a number of industrial processes — for example, the production of cements, of high-temperature refractories, and of slags for steel-making. It is now understood that the usefulness of solid oxides is increased if they are produced in forms of higher-than-normal chemical reactivity. Recent research at the Materials and Molecular Research Division (MMRD) of Lawrence Berkeley Laboratory and at the Chemistry Laboratory of the Faculty of Engineering, University of Genoa, Italy, shows that oxides of greatly increased activity can be produced by modifying conventional processing conditions.

Two ideas for new ways of producing active oxides were uncovered in the manner of detective fiction: one critical clue was a mysterious layer, buried inside a decomposing solid particle and too thin to see with the naked eye, while a second critical clue was a missing x-ray diffraction pattern. Both clues were discovered

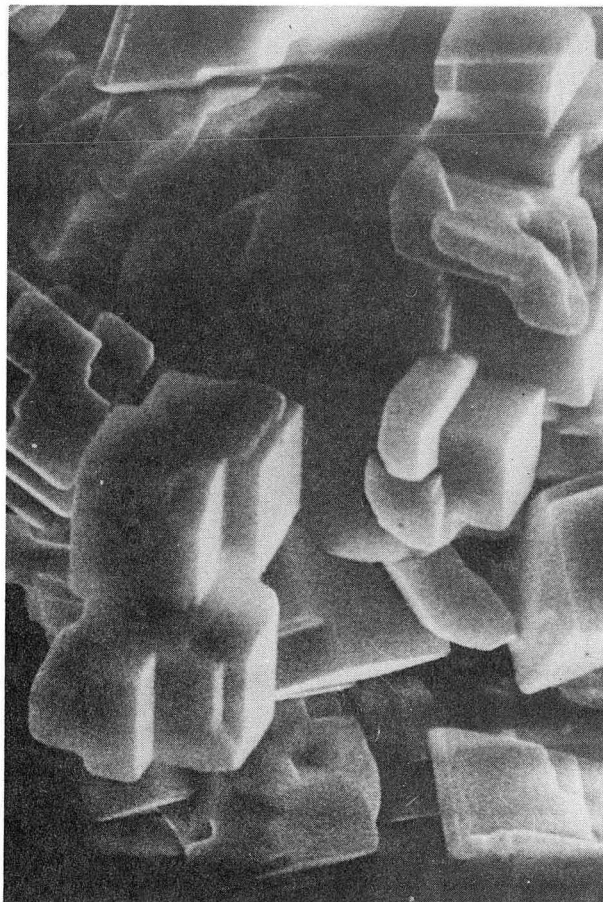


Figure 1. Scanning electron microscope (SEM) picture of CaCO_3 powder.

in the course of experiments designed to test a general theory of decomposition reactions, which was developed by Professor Alan W. Searcy of MMRD and the Department of Materials Science and Mineral Engineering and by Professor Dario Beruto of The University of Genoa.

A prominent example of a decomposition reaction is the decomposition of calcium carbonate (CaCO_3), found in nature as limestone, sea shells, marble, Iceland spar, etc., to yield solid CaO and CO_2 gas. Decomposition reactions often occur with no change in the apparent volume of the solid particles, despite the fact that the true volumes of the solid products, which can be calculated from their crystal structures, are sometimes only about half the volume of the reactants. Figure 1 shows the size and shape of CaCO_3 particles that yield the CaO particles of Figure 2. The CaO of these particles occupies only 45% of their apparent volume. The remainder of the apparent volume must be accounted for by pores, which either are obscured by the products of reactions of moisture or CO_2 at the particle surfaces or are smaller than the limit of resolution of the scanning electron micrograph (SEM), about $1\mu\text{m}$ (4×10^{-5} in.).

The slowest chemical step of a decomposition reaction can be a step on the reactant surface, as assumed in past theories, but it also can be solid state diffusion or the escape of the gaseous product through the very small pores in the solid product. The new theory deals with all these possibilities and with how they can be distinguished.

Knowledge of the pore geometry is required to interpret any effect of product layer thickness on decomposition rates. The gaseous reaction products usually do not pass out through the pores by the familiar mechanism of hydrodynamic flow. If pore diameters are less than $1\mu\text{m}$, molecules of a gas at pressures as high as 1 atmosphere seldom collide except at the pore walls. The resistance to escape of the gas through the pores can be predicted from the pore geometry.

In order to learn, if possible, the geometry of the pores through the CaO layer on CaCO_3 during decomposition in vacuum, single crystals of CaCO_3 were partially decomposed and then cut to expose a cross section for examination by the SEM and by x-ray diffraction. The SEM showed a $30\mu\text{m}$ (10^{-3} in) layer between macroscopic layers which could be identified from their x-ray diffraction patterns as undecomposed single crystalline CaCO_3 and oriented polycrystalline CaO (see Figure 3). The $30\mu\text{m}$ layer gave a single very broad x-ray diffraction peak.

That layer immediately became the center of intense study. Broad x-ray peaks are characteristic of amorphous solids, that is, solids which either are composed of very small crystals or are non-crystalline glasses. Theoretical considerations suggested that the layer was an amorphous form of CaO that is formed in vacuum by a process that is kinetically more favored than is formation of crystalline CaO but, when grown to more than a critical thickness, is transformed by accumulated strain to crystalline CaO .



Figure 2. SEM picture of the CaO particles produced by complete decomposition of the CaCO_3 of Figure 1.

The new theory for decomposition reactions shows that the reaction rate can be decreased if an amorphous solid is produced instead of the crystalline one. To clarify the kinetics it was necessary, therefore, to establish the properties of this amorphous layer, which appeared to be the direct product of the decomposition of CaCO_3 . Furthermore, amorphous oxides are always of higher chemical activity than are the corresponding crystalline oxides. Because CaO is used in more industrial applications than all but perhaps two other solid oxides, the discovery and isolation of a previously unknown amorphous form of CaO would be of great practical importance.

If the hypothesis is correct that the intermediate layer transformed to the stable oxide because of accumulated strains when its thickness exceeded $30\mu\text{m}$, the amorphous solid might be isolated by decomposing in vacuum CaCO_3 powder that had been ground to less than $30\mu\text{m}$ linear dimensions. In fact, a nearly noncrystalline form of CaO was produced by this means. Figure 4 compares the sharp x-ray diffraction pattern of the CaO produced by CaCO_3 decomposition in air or dry nitrogen to the pattern obtained by vacuum decomposition.

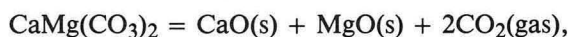
As expected, the poorly crystalline powder proved to react with liquid water, water vapor, or SO_2 gas much more readily than ordinary commercial CaO . With water vapor at 140°C , reaction is complete in three minutes, while samples of normal CaO are only 5% reacted in ten minutes.

Unfortunately, the active CaO cannot be produced in greater amounts simply by heating greater amounts

of CaCO_3 in vacuum. Both the surface area and the deviation from perfect crystallinity (as measured by the width of x-ray diffraction peaks) increase when samples of a fixed size are heated under conditions that reduce the time of exposure to the gaseous product of the reaction, CO_2 . Clearly, CO_2 catalyzes a decrease in surface area and conversion to more highly crystalline CaO . If the quantity of CaCO_3 is increased, the time of exposure of the CaO to CO_2 that escapes from the interior of the solid mass is increased and the activity of the CaO goes down.

Conventional CaCO_3 processing techniques cannot readily be modified to reduce CO_2 pressures in order to obtain the high surface area and low crystallinity that are the sources of the high CaO activity. Fortunately, fluidized bed processing, a technique in which powdered solids are suspended by a gas stream during reaction, may prove a commercially feasible means of obtaining, if not fully noncrystalline CaO , at least CaO of considerably lower crystallinity and higher surface areas than are now commercially available. A study of decomposition of CaCO_3 in a fluidized bed is being undertaken in Genoa.

Meanwhile back at MMRD, Elizabeth Knauf, now Elizabeth Powell, in the course of her research for the MS degree in ceramic engineering, discovered the second clue. Her carefully measured CO_2 pressures were inconsistent by a factor of 1000 with pressures calculated from well-established thermodynamic data for the reaction that previous investigators believed to occur:



where the s's indicate separate crystalline oxide products. Twenty years earlier similar anomalous results

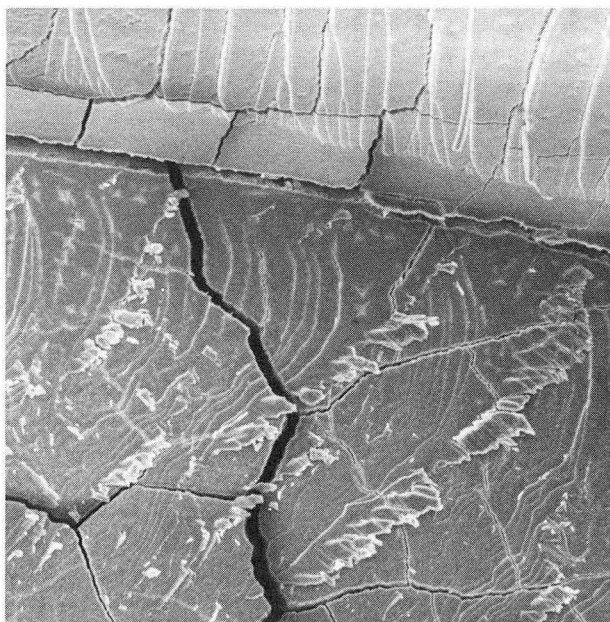


Figure 3. SEM picture of the $30\mu\text{m}$ layer that is present between undecomposed CaCO_3 and a growing layer of polycrystalline CaO during CaCO_3 decomposition in vacuum.

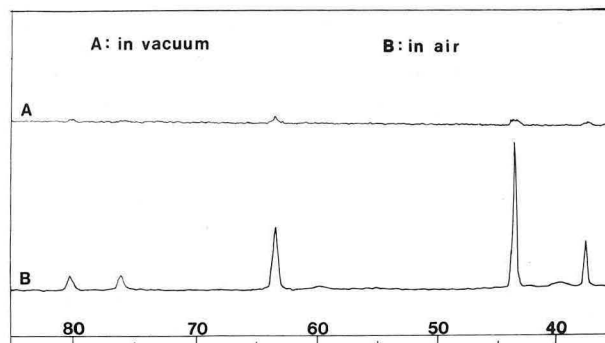


Figure 4. Comparison of the x-ray diffraction pattern of the CaO produced by decomposition of CaCO_3 in vacuum (pattern a) to the pattern obtained by decomposition in air or dry nitrogen (pattern b).

had been obtained in a study of $\text{Mg}(\text{OH})_2$ decomposition to $\text{MgO} + \text{H}_2\text{O}$ gas. These results were dismissed as reflecting an unidentified flaw in the method. But Ms. Powell found that, although x-ray diffraction patterns of CaO and MgO are found in samples of completely decomposed dolomite, only the diffraction pattern of dolomite could be found in a sample that was half decomposed. The x-ray patterns of CaO and MgO should have been clearly visible if crystalline CaO and MgO were present in initial stages of decomposition when the CO_2 pressures were measured.

The discrepancy in the pressure measurements for both dolomite and $\text{Mg}(\text{OH})_2$ decomposition are nicely explained by an assumption suggested by the missing diffraction patterns: The production of some amorphous solids is known to be possible only when impurities are present. It seems likely that until most of the CO_2 is driven out, the product of dolomite decomposition is a glass-like solid of higher activity than investigators have thought could be produced in high-melting oxides. Experiments are under way at MMRD that will prove or disprove these interpretations.

Basic research designed to clarify our understanding of the relationship between processing conditions and the activity of solid oxides from decomposition reactions continues. But exploration of possible practical applications of the discoveries to date has already begun. One of the most serious pollution problems facing modern industry is the removal of sulfur oxides from industrial stack gases. It is widely believed that the most practical means for removing these sulfur oxides may be to react them with the oxides produced by decomposing CaCO_3 or dolomite. Whether or not active forms of these oxides are more effective in this application is now under study. At Genoa, Beruto and his associates have obtained preliminary evidence that the substitution of active CaO for ordinary CaO improves the quality of slags used in steel-making. Professor P. Kumar Mehta of UC's Department of Civil Engineering, and Professor Richard Berger, a consultant to MMRD from the University of Illinois, are exploring the value of active CaO as a component of cements. There is reason to expect that the active CaO may significantly shorten the time required to achieve initial setting of cement pastes.

—Alan W. Searcy

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