Diffusion through $CaSO_4$ Formed during the Reaction of CaO with SO_2 and O_2

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In SO_2 emission control, CaO sorbent is commonly used to react with flue gas. The reactions lead to the formation of $CaSO_4$ on the CaO particles. The CaO sorbent is derived from either $CaCO_3$ or $Ca(OH)_2$, which decomposes at high temperature to produce highly porous and reactive CaO sorbent. During the conversion of CaO to $CaSO_4$, the pores in the CaO particles become plugged because there is a volume expansion of the solid with the reaction. With the formation of $CaSO_4$, further reaction has to continue by diffusion through the sulfate product layer. This becomes a major resistance in the sulfation reaction. Prior studies have resulted in various models to account for the observed reaction rates (Hartman and Coughlin, 1976; Hartman and Trnka, 1980; Bhatia and Perlmutter, 1981; Simons and Garman, 1986). Recently, it has been suggested that the sulfation reaction is controlled by transport through the $CaSO_4$ product layer, that is, by solid-state ionic diffusion (Bhatia and Perlmutter, 1981; Borgwardt et al., 1984, 1987). Further, it has been proposed that the migrating species in the solid $CaSO_4$ layer are $O^=$ and $SO_4^=$ with $CaSO_4$ formation at the $CaO/CaSO_4$ interface (Borgwardt et al., 1987). This, however, is not experimentally verified in prior work.

Solid-state reactions are usually heterogeneous. The reactants are commonly separated from each other by a newly formed solid product phase (Schmalzried, 1974). When the solid product phase is dense and not cracked, the reaction has to proceed by solid-state diffusion through the product layer. The transport mechanism of the reactants depends largely on the crystal structure and ionic nature of the product layer. For example, metal oxidation relies on ionic diffusion through the oxide layer between the metal and the gas phase (Rapp, 1984). In real crystals, the lattice always contains imperfections, and these defects make solid-state diffusion possible. Among crystalline defects, only point defects are thermodynamically stable and they are primarily responsible for solid-state diffusion at high temperatures (Schmalzried, 1974). In general, ionic mobilities increase with increasing defect concentration. To maintain electroneutrality within the crystal, the different defects have to balance electrically. Usually, one type of defect, which gives rise to the highest mobility, dominates the total transport process. The defect type and concentration are closely related to the electrical conductivity of the ionic solid.

Experimental Studies

To identify the dominant diffusing species in a solid-state reaction, marker experiments are often performed (Mrowec, 1980; Schmalzried, 1974). The marker method involves attachment of small inert marker particles to the solid at the original gas/solid interface. The inert marker material should not react or dissolve in the other phases of the system. As the transport and reaction proceed, the product layer forms and thickens on either side of the solid. Following some reaction, there are two limiting cases for the location of the markers. The direction of ionic species transport through the product layer influences the relative marker position. If the transport through the product layer is dominated by inward solid-state diffusion of the reactant species derived from the gas phase, the marker will remain at the solid product/gas reactant interface. This is called "inward growth mode," as shown in Figure 1a. On the other hand, if the transport is predominantly by the outward diffusion of reactant species derived from the solid reactant, the marker will be located at the solid reactant/solid product interface. This is called "outward growth mode," as shown in Figure 1b. The marker experiment technique has been used widely in the studies of oxidation of metals (Mrowec, 1980; Rapp, 1984).

In this work, platinum markers were used in the CaO-O_2-SO_2 system to characterize the dominant transport process and the growth mode of the $CaSO_4$ product layer. Pure CaO powder (Aldrich Chem., 99.95%) was dry-pressed into tablets of 10-mm diameter and 4-mm thickness. The tablets were sintered

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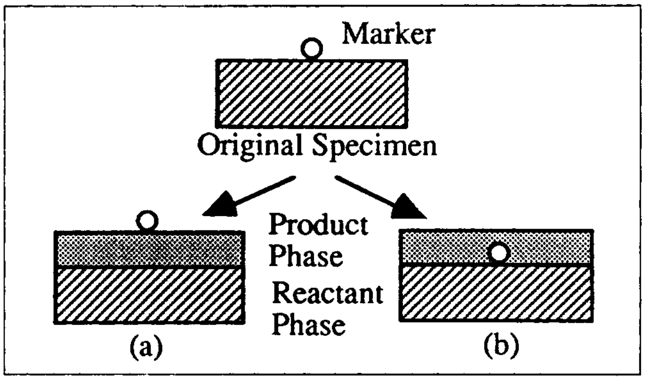

Figure 1. (a) Inward growth where reactants move from gas/solid interface to solid/solid interface; (b) outward growth where reactants move from solid/solid interface to gas/solid interface.

in air at 1,400°C for 24 hours in a tube with SiC resistance heating elements. After cooling to room temperature, the CaO tablets were removed from the furnace, and three strips of Pt paste (Engelhard) were applied to one side of each tablet. The Pt paste was composed of fine Pt powder, terpineol, and other organic solutions. The terpineol and the organic solutions were burned off at high temperatures, leaving a thin layer of Pt on the surface of each CaO tablet. The thin strips of Pt served as the markers. The CaO tablets were placed in the reaction tube furnace, and a gas mixture of SO_2 (5,000 ppm)/air was passed through the tube at 60 mL/min. The CaO tablets were maintained at 1,300°C in the reactive gas for 30 days.

When the sulfation reaction were terminated, one of the tablets was ground into powder for X-ray diffraction analysis (XRD). Another tablet was mounted in epoxy resin. The cross section of the mounted tablet was polished and then examined under a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS) analytical system. Sulfur mapping by EDS was performed to identify the $CaSO_4$ product phase. The results are presented in micrographs in the following section.

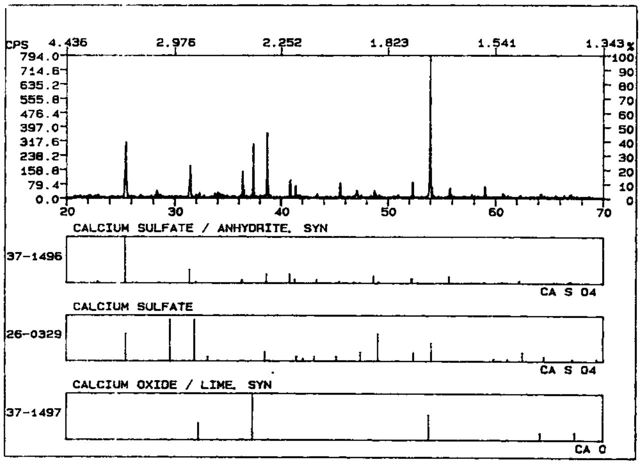

Figure 2. Diffraction pattern of a partially converted CaO tablet.

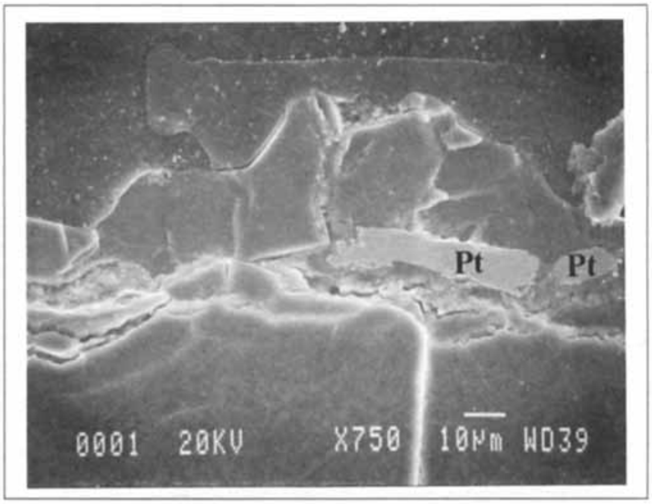

Figure 3. SEM micrograph of the cross section of a partially converted tablet.

Results and Discussion

The result of the XRD is shown in Figure 2. The peaks of the diffraction pattern show that the tablet was composed of $CaSO_4$ and CaO. This indicates that the tablet was partially converted. Figure 3 is a micrograph of the cross section of a partially transformed tablet. In Figure 3, as marked on the micrograph, the Pt markers are imbedded within the solid phases. The contrast between the solid phases, however, is not very clear, and a careful compositional analysis was crucial. Figure 4a is a computer-processed image of Figure 3. Figure 4b shows the sulfur mapping of the region in Figure 4a. In EDS sulfur mapping, a region with high sulfur content gives off signals which appear as a bright area on the micrograph. The higher the sulfur content, the greater is the brightness. From Figure 4b, it is clear that the Pt markers are located between the high sulfur region ($CaSO_4$) and the low sulfur region (CaO). This corresponds to the case of "outward growth mode" discussed previously. Therefore, the reaction system proceeds in part by outward diffusion of Ca^{++} ions through the product layer. At the $CaSO_4$/gas interface, Ca^{++} ions react with the gaseous species to form $CaSO_4$. It is a further re-

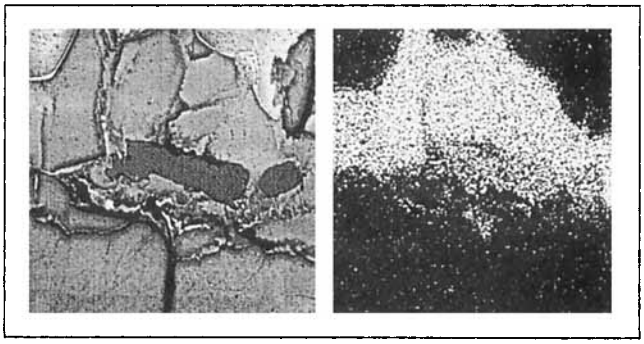

Figure 4. Computer-processed image of the cross section of specimen in Figure 3 (left); (b) sulfur mapping of the cross section with Pt marker located between CaO and $CaSO_4$ (right).

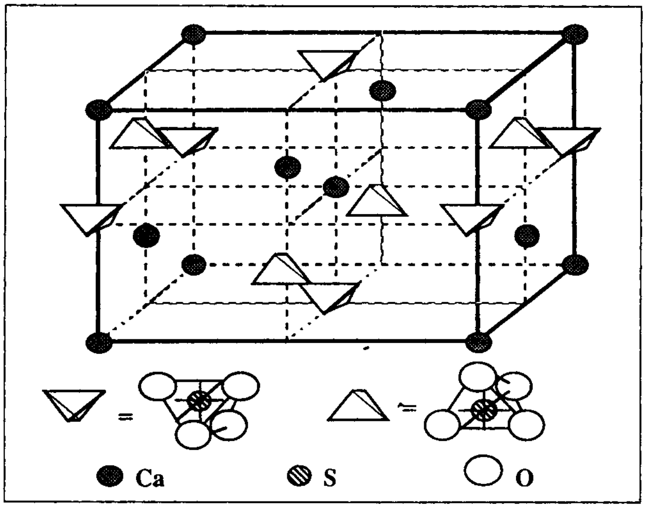

Figure 5. Crystal structure of $CaSO_4$.

quirement that $O^=$ must migrate in a coupled manner with Ca^{++} to satisfy local mass and charge balances.

To understand ionic diffusion in solids on an atomisitic scale, a review of the relevant crystal structure is helpful. Figure 5 shows the crystal structure of $CaSO_4$ (Wyckoff, 1960). The tetrahedra represent the complex $SO_4^=$ ions, and the dark circles represent the Ca^{++} ions. When the upper half of the lattice is "removed," the top view of the remaining lattice appears as shown in Figure 6. The $SO_4^=$ tetrahedra are outlined with dashed lines. The bonding between sulfur and oxygen is covalent in nature (Evans, 1964), which makes the breaking away of either sulfur or oxygen difficult. Moreover, the size of the complex $SO_4^=$ ion is much greater than that of the Ca^{++} ion (roughly 4.5 Å vs. 1.8 Å, Evans, 1964). This means that the Ca^{++} ions inherently have a higher mobility than the $SO_4^=$ ions. This examination of the crystal structure supports the result obtained from the marker experiment described previously. The mechanism of associated $O^=$ transport, however, needs to be clarified. A plausible explanation is that the dissolution of CaO in $CaSO_4$ creates vacancies on some of the $O^=$ sites in the tetrahedra, thereby enhancing the mobility of the $O^=$ ions to jump from one tetrahedron to the other. Thus, Ca^{++} and $O^=$ can move in a coordinated manner to the $CaSO_4$/gas interface. At the solid/gas interface, $CaSO_4$ formation reaction occurs:

$$Ca^{++} + O^= + SO_{2(g)} + \frac{1}{2} O_{2(g)} = CaSO_{4(s)} \qquad (1)$$

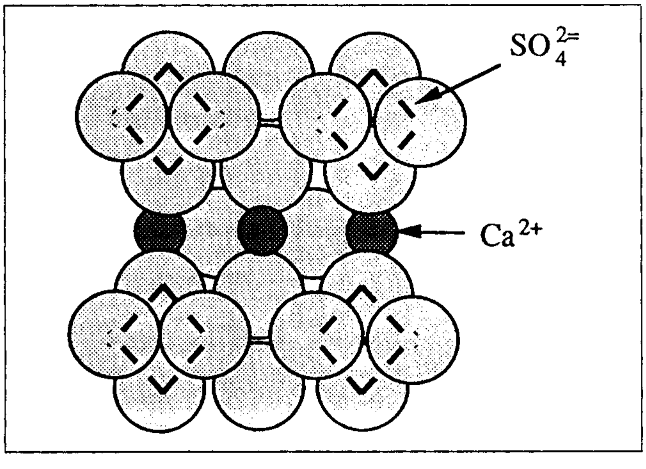

Figure 6. Top view of the bottom half of $CaSO_4$ lattice in Figure 5.

In the prior literature it has been supposed that $SO_4^=$ ions are formed at the $CaSO_4$/gas interface and then migrate through the $CaSO_4$ product layer to the CaO/$CaSO_4$ interface (Borgwardt et al., 1984, 1987). Their suggestion is inconsistent with our experimental findings. Further, the relative ionic mobility of such a large ion is known to be very low. From the above discussion, it is therefore concluded that Ca^{++} and $O^=$ ions diffuse through the $CaSO_4$ product layer to the $CaSO_4$/gas interface, and the reaction proceeds at a rate limited by such transport of Ca^{++} and $O^=$. Further determination of the ionic mobilities, transport characteristics, and electrical properties in $CaSO_4$ is in progress.

Acknowledgment

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