Ca-Mg Acetate as Dry SO_2 Sorbent: II. Sulfation of CaO in Calcination Product

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The sulfation rate of CaO contained in calcined calcium magnesium acetate CMA by SO_2 and O_2 was measured. Although calcined CMA contains CaO and MgO, only CaO reacts with SO_2 above 950°C. The reaction occurs at a much greater rate than with other conventional desulfurization agents like calcined limestone, dolomite, or $Ca(OH)_2$, the last of which yields one of the most reactive forms of CaO. The remarkable enhancement of sulfation rate of CaO in calcined CMA is due to its much larger pore size and porosity than those of other agents. Another consequence of this structure of calcined CMA is that the sulfation reaction proceeds to completion without the rate leveling off, unlike in the sulfation of most oxides.

Introduction

The reactivity of the calcination product of calcium magnesium acetate (CMA) as a possible dry desulfurization agent has been investigated. The first step in the dry desulfurization reaction is the thermal decomposition of CMA, which was studied in detail in Part 1 of this series (Han and Sohn, 2002). Part II presents the kinetics of the sulfation reaction of CaO in calcined CMA with sulfur dioxide in the presence of oxygen. The thermodynamic considerations will be presented first, followed by the results of kinetics measurements. The sulfation of an MgO component that occurs in a different temperature range and follows a different mechanism will be described in Part III of this series (Sohn and Han, 2002). Information on the separate sulfation of the two oxides is required to describe the overall sulfation rate of calcined CMA under any conditions, because their sulfation rates have different dependencies on temperature and other conditions.

Thermodynamic Considerations

In this section, the possible product phases obtained when pulverized CMA is injected into a coal-fired boiler to react with sulfur dioxide under typical operational conditions are examined thermodynamically. The analysis was performed by the use of the HSC Chemistry (version 2.03) software developed by Outokumpu Research Oy of Finland, which has a built-in thermodynamic database.

Phase equilibria

CaS, $CaSO_3$, and $CaSO_4$ were considered as the possible phases for the reaction of CaO with SO_2 in the presence of oxygen, and MgS and $MgSO_4$ were considered as the possible product phases with respect to MgO. Figure 1 shows the phase equilibria for the sulfation of CaO under fixed temperatures: the solid line at 700°C and the dashed line at 1,100°C. The crosshatched box in the figure indicates the typical operational conditions of a coal-fired boiler. As shown, the only stable product of CaO sulfation is $CaSO_4$ at both temperatures. Figure 2 represents the phase equilibria of MgO sulfation, the solid and the dashed lines showing the equilibria at 700°C and 1,100°C, respectively. The crosshatched box in the figure indicates the normal operational conditions of a coal-fired boiler. In this case, $MgSO_4$ is the stable phase at 700°C, but MgO (not $MgSO_4$) is stable at 1,100°C

Equilibrium partial pressure

Based on the above thermodynamic considerations, the main reactions of CaO and MgO with sulfur dioxide in the

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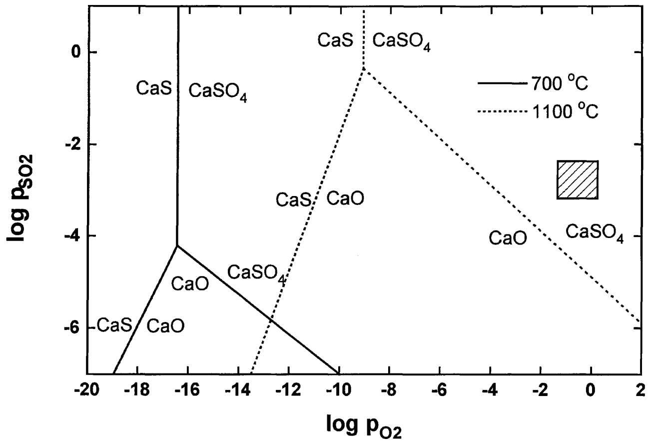

Figure 1. Stability of Ca-S-O system.

p_{SO_2} and p_{O_2} are in atm.

presence of oxygen are expected to be

$$CaO + 1/2O_2 + SO_2 = CaSO_4 \tag{1}$$

$$MgO + 1/2O_2 + SO_2 = MgSO_4 \tag{2}$$

The two oxides within calcined CMA are fine crystalline grains, and, thus, cannot be separated physically. Thus, they must be sulfated separately in each other's presence to determine the kinetics of individual sulfation reactions. The equilibrium partial pressure of sulfur dioxide of each sulfation reaction was calculated to determine the conditions under which they are sulfated separately.

Since the oxide and the sulfate form separate pure phases, the equilibrium relation for Reaction 1 as well as that for 2 can be expressed by

$$p_{SO_2} = \frac{1}{K \cdot p_{O_2}^{1/2}} \tag{3}$$

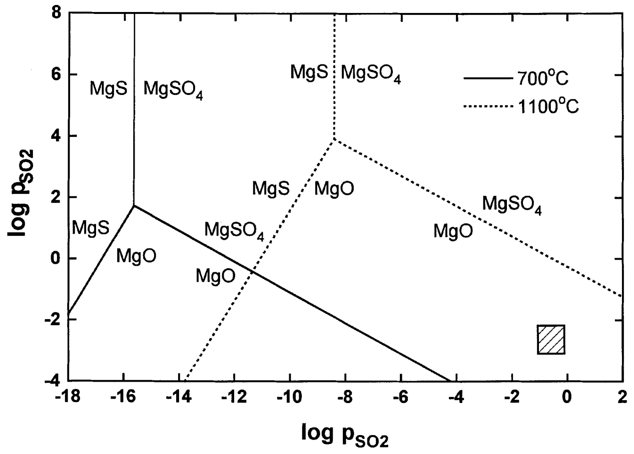

Figure 2. Stability of Mg-S-O system.

p_{SO_2} and p_{O_2} are in atm.

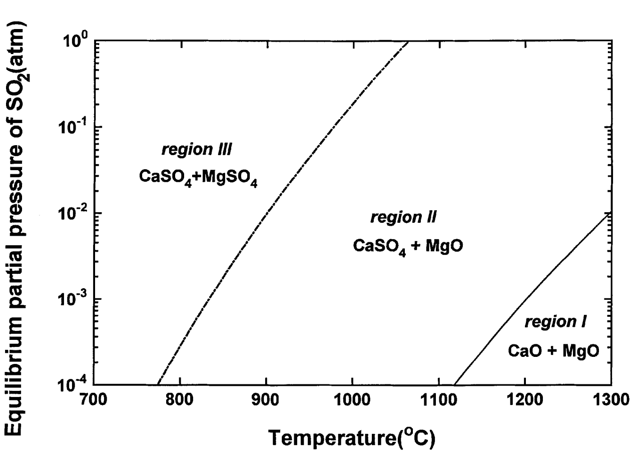

Figure 3. Equilibrium SO_2 partial pressure (in atm.) vs. temperature for the sulfation of CaO and MgO at 4.3 kPa oxygen partial pressure.

where the partial pressures are relative to one atmosphere pressure, that is, in atm unit.

Thus, the equilibrium concentrations of sulfur dioxide for Reactions 1 and 2 are functions of temperature and oxygen concentration. Figure 3 was prepared from the thermodynamic relations under a fixed oxygen partial pressure of 4.3 kPa (5% by volume under the atmospheric pressure of 86.1 kPa in Salt Lake City), which is the approximate oxygen content in a typical power plant flue gas. The solid line in Figure 3 shows the equilibrium pressure of SO_2 with respect to Reaction 1. Similarly, the dashed line displays the equilibrium pressure of SO_2 for Reaction 2. In this system, there exist three regions divided by two equilibrium lines. In region I, the partial pressure of SO_2 is below the equilibrium value for Reactions 1 and 2 and, thus, these reactions are not feasible thermodynamically. Region II is located between the solid line and the dashed line. The partial pressure of SO_2 in this region is above the equilibrium value for Reaction 1 and simultaneously below the equilibrium pressure of SO_2 for Reaction 2. Therefore, only CaO reacts with SO_2. In region III (above the dashed line), both CaO and MgO can react with SO_2.

Experimental Work

A thermogravimetric analysis (TGA) unit consisting of three major parts—an electrobalance, a reactor, and a gas-delivery system—was used in this work (Han and Sohn, 2002; Han, 1998). The weight changes taking place during the reaction were measured continuously with a Cahn balance (Model 1000). In the course of the experiment, the balance chamber was purged continuously with nitrogen gas to prevent the intrusion of reaction gas and heat. The furnace tube was an Inconel pipe with 66.0 cm length and 5.1 cm ID. One-fifth of the reactor was filled with ceramic balls for mixing and preheating of the inlet gases. An R type thermocouple (platinum vs. platinum + 13% rhodium) was protected in a 0.6 cm diameter ceramic tubing and positioned adjacent to the sample within the reactor. A sample tray made of alumina, 2.6 cm ID

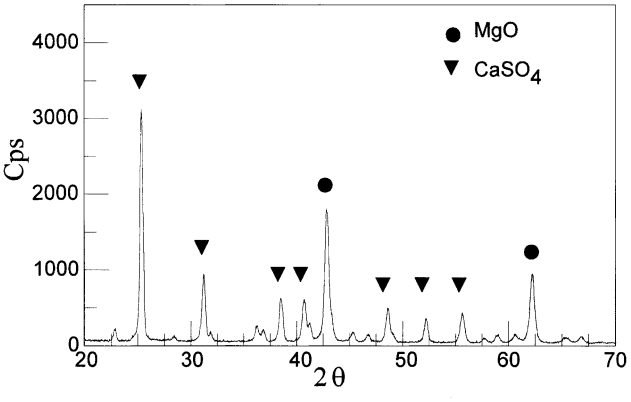

Figure 4. XRD pattern of the CaO sulfation product.

and 0.4 cm depth, was suspended into the uniform temperature zone of the reactor with a platinum wire.

In the determination of intrinsic particle kinetics parameters, it is important to ensure that measurements are carried out under the conditions such that diffusion between and within the particles and external mass transfer do not affect the overall rate. The particle size of CMA used for this purpose was small and the porosity of calcined CMA was high, as discussed in Part I of this series. The effect of interstitial diffusion was removed by charging a 300 mg sample as a thin layer to minimize the diffusion path. Gas-flow rates in the range of 0.6 to 1.81 NL/min were used to investigate the effect of gas-flow rate (using calcined CMA powder of $-325+400$ mesh in 0.5% SO_2 in the presence of 5% oxygen at 1,000°C). It was determined that the reaction rate was independent of the flow rate above 1.5 NL/min (Han, 1998). Thus, in all the subsequent runs, a gas-flow rate of 1.8 NL/min was chosen to avoid any external mass-transfer effects. The exit gas was cleaned by bubbling it through a 10% hydrogen peroxide solution in water to remove unreacted sulfur dioxide before being discharged. Drierite dehydration units were placed just before the flow meters to remove moisture from the gases. Anhydrous grade (minimum 99.9% purity) sulfur dioxide was supplied by Union Carbide. Nitrogen and oxygen were supplied by Air Product Co. and had a minimum 99.9% purity.

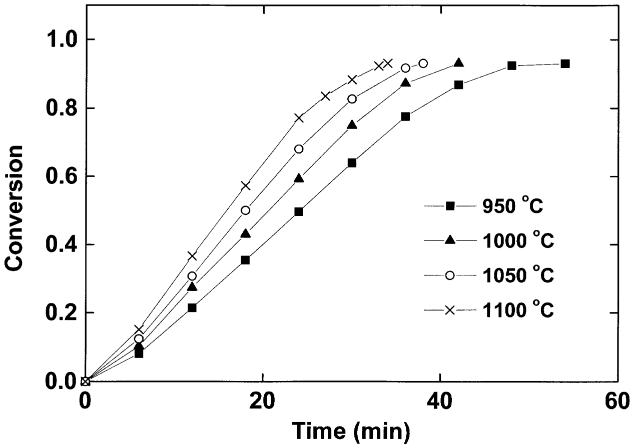

Figure 5. Effect of temperature on CaO conversion.

$p_{SO_2} = 0.43$ kPa; $p_{O_2} = 4.3$ kPa.

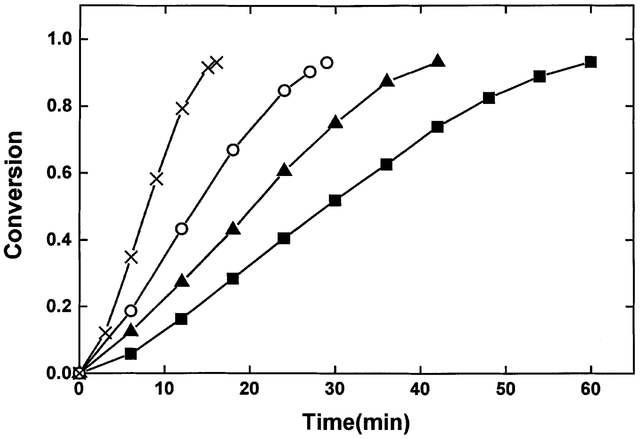

Figure 6. Effect of SO_2 partial pressure on CaO conversion.

$p_{O_2} = 4.3$ kPa; $T = 1,000$°C. ■ 0.26 kPa; ▲ 0.43 kPa; ○ 0.61 kPa; × 0.86 kPa.

Experimental Results

Intrinsic rate of CaO sulfation

To determine the kinetics of just the CaO sulfation, the calcined CMA samples were reacted under region II conditions in which only CaO can be sulfated.

Effect of Reaction Temperature. The influence of temperature on Reaction 1 was examined in the range 950 to 1,100°C. In these runs, the partial pressures of SO_2 and O_2 were kept constant at 0.43 and 4.3 kPa (0.5 and 5 vol. %), respectively. As discussed earlier, the product phase should be $CaSO_4$ and MgO under these conditions, which was verified by XRD analysis (Siemens Model D5000 using Cu Kα line) as shown in Figure 4. The experimental results for CaO conversion are shown in Figure 5.

Effect of Sulfur Dioxide Partial Pressure. The partial pressure of sulfur dioxide ranged from 0.26 to 0.86 kPa (0.3 to 1 vol. %) for this study, while maintaining the total flow of sulfur dioxide, oxygen, and nitrogen at 1.81 NL/min. The temperature of the system and the content of oxygen were kept at 1,000°C and 4.3 kPa (5%), respectively. The results for CaO conversion under various sulfur dioxide partial pressures are shown in Figure 6.

Attainment of high degrees of conversion

The product sulfates have much larger molar volumes than the corresponding oxides, by a factor of 2.7 for the sulfation of CaO. Thus, typical sulfation rates level off as the reaction proceeds due to the formation of a dense product layer (Chang and Thodos, 1984; Hajaligol et al., 1988; Kim, 1999), even when the reactant oxide has some initial porosity. It is, therefore, of great interest to note that the sulfation of CaO in the calcined CMA does not level off even at high conversion levels. This has an important implication in that all of

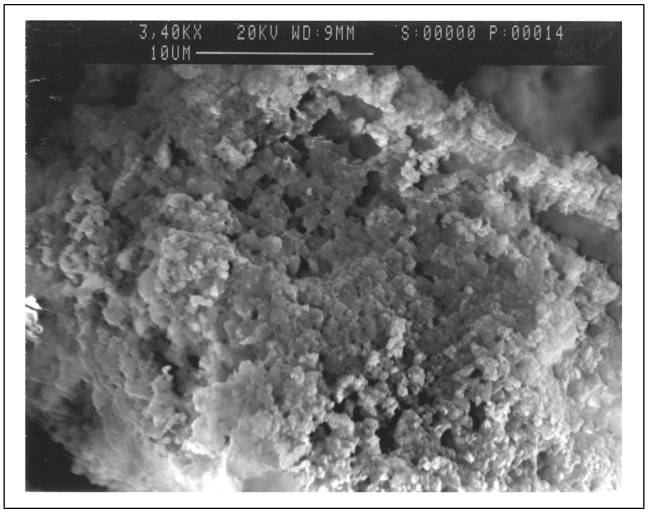

Figure 7. Scanning electron micrograph of unplugged pores after CaO sulfation.

the CaO in the calcined CMA can be utilized for SO_2 removal, thus, making its sulfation capacity high. When CMA decomposes, it loses a large amount of matter as gases, leaving a highly porous product with a popcorn-like structure with thin porous walls pierced with large blowholes, as shown by a scanning micrograph presented in Part I of this series. These large pores (5–50 μm) not only provide a large interior surface area, but also serve as SO_2 pathways to the interior of the particles that promote high absorbent utilization. When limestone is calcined at various temperatures from 750°C to 1,100°C, the main peak having the largest pore size in the differential pore-size distribution curve appears at 950°C with the pore diameter of around 1 μm (Dogu, 1981). Dam-Johansen and Ostergaard (1991) carried out the calcination of 23 limestones at 850°C and determined the maximum pore sizes to range from 0.1 to 1 μm. With the very open microstructure, the calcined CMA keeps much porosity and internal surface area when sulfated, as shown in Figure 7. As a result, the sulfation rate of the CaO in the calcined CMA does not level off until complete conversion.

Analysis of Rate Data

For reactions in which the product solid occupies a greater volume than the reactant solid, the pore blocking model (Evans, 1960; Kim, 1999; Won and Sohn, 1985) usually fits the reaction rate. In such reactions, the rate is initially rapid and levels off at less than complete conversion because of pore pluggage. As indicated in the previous section, however, in the case of the sulfation of calcined CMA, the pores do not become plugged in spite of the solid volume increase. The following nucleation-and-growth kinetic equation was found to yield the best fit of the experimental data

$$[-\ln(1-\alpha)]^{1/m} = k_{\text{app}}t \tag{4}$$

where α is fractional conversion, m is a constant, and k_{app} is the apparent rate constant which is given by

$$k_{\text{app}} = k \cdot f(p_{SO_2}) \tag{5}$$

where k is the rate constant, p_{SO_2} is the sulfur dioxide partial pressure, and f designates the partial pressure dependence of rate. The rate constant k is related to temperature by

$$k = k_o \cdot \exp\left(-\frac{E}{RT}\right) \tag{6}$$

where k_o is the pre-exponential factor, E is activation energy, R is gas constant, and T is absolute temperature. It is apparent from Eq. 4 that a plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln(t)$ should be linear with m as the slope and $m\ \ln(k_{\text{app}})$ as the intercept with $\ln(t) = 0$.

The data shown in Figure 6 were plotted according to Eq. 4 to determine the effect of SO_2 partial pressure of Reaction 1. Straight lines through the data obtained by linear regression analysis had slopes between 1.48 and 1.83. Experimental data could be fitted up to about 90% conversion with an av-

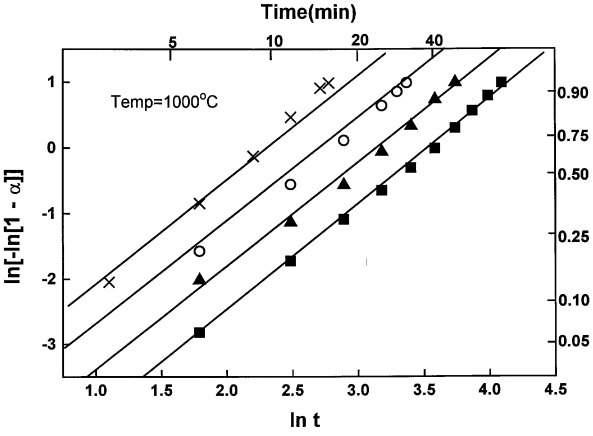

Figure 8. Plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln(t)$ according to Eq. 4 from the results in Figure 6.

■ 0.26 kPa; ▲ 0.43 kPa; ○ 0.61 kPa; × 0.86 kPa.

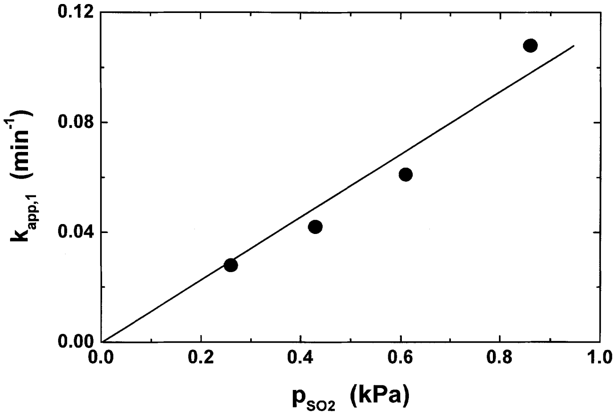

Figure 9. Dependence of the apparent rate constant on SO_2 partial pressure for CaO sulfation.

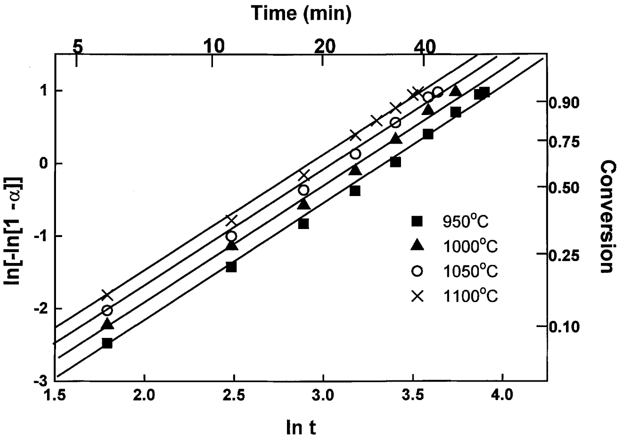

Figure 10. Plot of ln[$-$ln(1 $-$ α)] vs. ln (t) according to Eq. 4 from Figure 5.

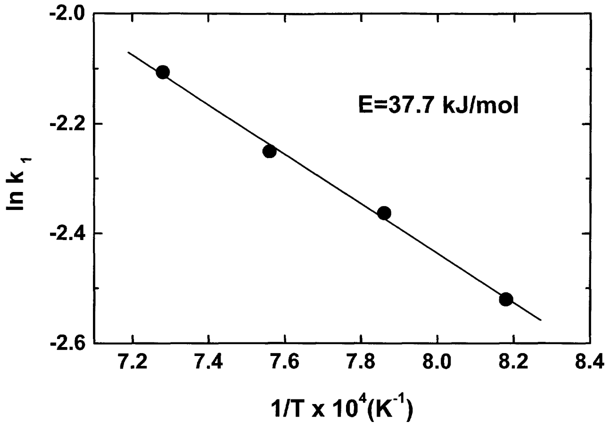

Figure 11. Arrhenius plot for the rate constants for CaO sulfation.

The units of k_1 are in $\text{kPa}^{-1} \cdot \text{m}^{-1}$.

erage value of slopes ($m = 1.65$), as shown in Figure 8. The values of $k_{\text{app},1}$ obtained from the intercepts are plotted in Figure 9 against the sulfur dioxide partial pressure. Although some scatter is present, a reasonable overall linear relationship is observed over the p_{SO_2} range of 0.26 to 0.86 kPa tested in this work. A first-order rate expression is convenient for rate analysis and for its application to the analysis of the reaction system when mass-transfer effects are significant. A more exact, but less convenient, rate equation is not likely to improve the prediction of intrinsic chemical kinetics of most gas-solid reactions because of the ever-present variability in the characteristics of fine solid particles that affect their reactivity. Thus, the best-fit straight line going through the origin was used for the rate analysis in this work. Based on Eq. 5, the slope of the straight line in Figure 9 corresponds to the rate constant k at that temperature.

Figure 10 shows a plot of ln [$-$ln(1$-$ α)] vs. ln t obtained from the results of Figure 5. The average value of the slope was 1.65 ($\pm$1.2%). This value of m agrees well with the average value obtained from the data on the sulfur dioxide concentration dependency. The values of k at different temperatures were obtained, as described above, from the intercepts in Figure 10 together with $f(p_{SO_2}) = p_{SO_2}$ in Eq. 5. The temperature dependency of k was plotted according to Eq. 6 as shown in Figure 11, yielding an activation energy of 37.7 kJ/mol. Combining all the above information, the equation for the intrinsic kinetics, unaffected by mass and heat transfer, of the CaO sulfation is, thus, represented by

$$[-\ln(1-\alpha)]^{1/1.65} = k_{\text{app},1} \cdot t \qquad (7)$$

where

$$k_{\text{app},1} = 3.26 p_{SO_2} \exp(-E/RT) \quad \text{min}^{-1} \qquad (8)$$

and $E = 37.7$ kJ/mol and p_{SO_2} is in kPa. As discussed below, oxygen partial pressure does not affect the rate in a typical range encountered in a dry desulfurization process (Simons et al., 1988), and, thus, does not appear in the rate equation.

It is noted that the pre-exponential factor obtained in this work is for the CaO sample obtained by the thermal decomposition of CMA under the heating schedules presented in Part I of this series. Being dependent on the specific surface area, the pre-exponential factor may vary with the heating schedule for the CMA decomposition if substantially different from that used in this work. Much higher heating rates in many industrial systems are expected to produce CaO with smaller pores and higher specific surface area resulting in higher reactivities. If the sample remains at high temperatures before being sulfated, its surface area and, thus, reactivity will be reduced. The activation energy, however, is expected to remain largely unaffected.

Comparison of SO_2 Removal Data from Various Sources

Marsh and Ulrichson (1985) reported that the sulfation of CaO derived from calcium hydrate is of first order with respect to SO_2 concentration with an activation energy of 79.8 kJ/mol. Borgwardt (1970) observed that a first-order chemical reaction was the rate-controlling step for the sorption of SO_2 by small particles of CaO, and the activation energy, which depended on the type of stone, ranged between 34.0 and 76.0 kJ/mol. The reaction rate was also found to be essentially independent of particle size (less than 0.5 mm) (Borgwardt, 1970) and oxygen partial pressure (Simons et al., 1988).

The reactivities of CaO samples from various sources were compared with those of CaO in calcined CMA. It is known that water vapor greatly increases the sulfation rate—up to 2–3 orders of magnitude at moderate partial pressures (Klingspor et al., 1983), which indicates the fact that a great deal of care must be taken when comparing the reactivities of different sulfur dioxide sorbents. Thus, only those data obtained in the absence of water vapor in the gas phase, as was the case in this work, were selected for comparison. The comparison was made at 900°C and a fixed partial pressure of sulfur dioxide of 0.26 kPa. As discussed above, only CaO is expected to react with SO_2 at 900°C. The source materials compared were CMA, $Ca(OH)_2$, Tymochtee dolomite, Greer

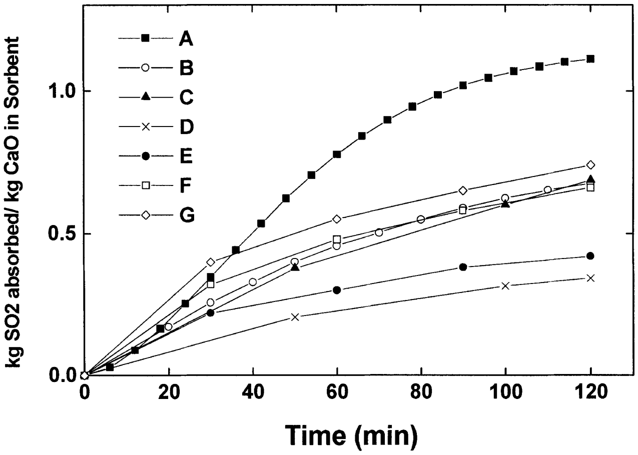

Figure 12. Comparison of the reactivity of CaO obtained from various sources.

p_{SO_2} = 0.26 kPa; p_{O_2} = 4.3 kPa; T = 900°C. A = CMA; B = $Ca(OH)_2$; C = Tymochtee dolomite; D = Greer limestone; E = Iceland spar limestone; F = Rigsby limestone; G = Fredonia limestone. (A and B from this work; C and D from Chang and Thodos (1984); E, F, and G from Hajaligol et al. (1988)).

limestone, Iceland spar limestone, Fredonia limestone, and Rigsby limestone. The first two materials were calcined and reacted in this work, whereas the data for the others were obtained from the literature (Chang and Thodos, 1984; Hajaligol et al., 1988). Before sulfation, $Ca(OH)_2$ was calcined to CaO under the same conditions as CMA. As shown in Figure 12, the sulfation rate of the CaO from CMA is much higher than that of CaO from other sources. Furthermore, the CaO from CMA absorbs a much greater amount of SO_2 than that from other sources before the rate levels off. As seen in the figure, the reactivity of the CaO from CMA is the highest followed by that from Fredonia limestone. The amount of SO_2 absorbed based on 1 kg of CaO by the calcined DMA was 0.78 kg after 60 min whereas that from Fredonia limestone was only 0.55 kg.

Since the work reported in this series of articles was completed, there have been articles published in the literature that deal with making reactive CaO by first reacting lime (Wu et al., 2002) with acetic acid and water followed by calcination. A comprehensive rate analysis was not performed in that work. Furthermore, a comparison of the reactivity of the resultant CaO with that of the sample tested in this work cannot be made because they used a reactant gas mixture that contains water vapor, which greatly increases the sulfation rate, as mentioned above (Klingspor et al., 1983). The pore size of their sample calcined at 800°C for 1 h was less than 4 μm, compared with 5–50 μm for CMA calcined at 10°C/min from 275 to 1,000°C in this work.

Concluding Remarks

The reactivity of calcined calcium magnesium acetate (CMA) as an SO_2 absorbent has been investigated. A Chevron ICE-B-Gon Deicer with an atomic ratio of Ca to Mg of 3 to 7 particle size of −325 + 400 mesh was used as the sample. Thermodynamic calculations revealed that there exist three regions for reaction feasibility: region I where neither CaO nor MgO is sulfated, region II in which only CaO is sulfated to $CaSO_4$, and region III where both oxides are sulfated.

Separate sulfation kinetics of CaO were determined in this work, and the following important results were obtained:

(1) The intrinsic sulfation rates of calcined CMA unaffected by mass-transfer processes are substantially higher than those of other desulfurization agents like calcined limestone and dolomite, because of the large internal surface area.

(2) The sulfation rates of CaO in calcined CMA remain relatively undiminished up to high levels of conversion (unlike those of other desulfurization agents), which results in its high utilization efficiency. This is because the pore size and porosity of calcined CMA are much larger than those of other materials, thus, minimizing the effect of solid volume increase upon sulfation. This is an important factor that contributes to the high desulfurization capacity of calcined CMA.

A pseudo-first-order kinetics expression is applicable for the sulfation of calcium oxide in calcined CMA. The reaction is of first order with respect to sulfur dioxide partial pressure. The CaO sulfation has an activation energy of 37.7 kJ/mol in the temperature range 950–1,100°C.

It is also stressed that a great deal of care must taken when comparing the reactivities of different sulfur dioxide sorbents in terms of the effect of reactant gas composition, because the sulfation rates depend very strongly on the water vapor content (Klingspor et al., 1983).

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