Calcined Calcium Magnesium Acetate as a Superior SO_2 Sorbent: I. Thermal Decomposition

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The reactivity of the calcination product of calcium magnesium acetate (CMA) as a possible dry desulfurization agent was evaluated. The first step in the dry desulfurization reaction—the thermal decomposition of CMA—was investigated by determining the decomposition reaction in three steps: 1. the evaporation of water starting at 65°C, 2. the conversion of CMA into $CaCO_3$ and MgO starting at 275°C, and 3. the decomposition of $CaCO_3$ to CaO starting at 580°C. The pseudo-first-order kinetic equation was observed for the CMA decomposition to $CaCO_3 + MgO$, with an activation energy of 165.5 kJ/mol. The decomposition of $CaCO_3$ to CaO also obeyed the pseudo-first-order kinetics, with an activation energy of 200 kJ/mol. As discussed in Part II of this series, the calcination product from CMA is quite reactive due mainly to the large porosity and internal surface area generated on the removal of the acetate group during the decomposition reaction. Furthermore, as will be shown in Parts II and III, the sulfation capacity of the calcined CMA is much greater than that of conventional sorbents because its sulfation rate does not level off until complete conversion and its MgO content is also sulfated at temperatures lower than about 900°C.

Introduction

The emission of large quantities of sulfur dioxide into the air from the coal power generating plants has been recognized as a long-term environmental and health hazard. A great deal of interest has been directed to developing more effective technologies to control the emission of sulfur dioxide. The most popular method for desulfurization is to react sulfur dioxide with basic solid oxides, such as calcined limestone or dolomite, to form stable sulfates. Generally, there are two types of technologies for desulfurization: post-combustion technologies and combustion zone technologies. Many facilities use the former, including the wet scrubber technology because of their efficiencies in spite of their high costs of installation and operation. On the other hand, the combustion zone technology using dry absorbent injection has the advantages of lower cost and simplicity, but it cannot satisfy the emission regulation by itself. It is, thus, used only for old and small plants, or in combination with different methods. However, if an absorbent that can satisfy the required efficiency is found, it is certain that the combustion zone technology would receive much attention because it has many advantages compared with the post-combustion technologies.

In the present study, the reactivity of calcined calcium magnesium acetate (CMA) as an SO_2 absorbent was investigated. Although there is a large amount of work related to the sulfation of limestone or dolomite (Cole et al., 1985; Hartman and Tranka, 1980; Klingspor et al., 1983; Qin, 1995; Reid, 1970; Wen and Ishida, 1973; Wiedemann et al., 1990; Yen et al., 1981), little is known about the dry sulfation of calcined CMA. CMA is a deicing salt less corrosive than chlorine based salts, and is already established by the U.S. Federal Highway Administration as the road salt selected to replace chlorine-based deicers. The chemical structure of CMA ($Ca_mMg_n(CH_3COO)_{2(m+n)}$) is similar to that of dolomite ($CaMg(CO_3)_2$). Like dolomite, CMA readily decomposes into CaO and MgO by heat. The evolution of gases during the decomposition of CMA leaves the solid product very porous with a large internal surface area. Thus, it was thought that calcined CMA would make a promising absorbent for SO_2 gas. Since the work reported in this series of articles was completed, there have been articles published in

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the literature that deal with making reactive CaO by first reacting lime (Sasaoka et al., 1998; Wu et al., 2002) or limestone (Sasaoka et al., 1997) with acetic acid and water followed by calcination. Other investigators studied the activation or reactivation of SO_2 sorbents by hydration (Al-Shawabkeh et al., 1997; Laursen et al., 2001) or aqueous-phase carbonation (Agnihotri et al., 1999).

In Part I, the experimental results for the thermal decomposition of CMA prior to the reaction with sulfur dioxide are discussed, including the decomposition path and detailed kinetics of the reaction. The sulfation rates and capacities of the decomposition products, both of which are much higher than those of conventional sulfur dioxide sorbents, are discussed in Parts II and III of this series (Sohn and Han, 2002a,b).

Experimental Apparatus and Procedure

Apparatus

A thermogravimetric analysis (TGA) unit, which is often and conveniently used to study gas-solid reactions (Han, 1998; Szekely et al., 1976), consisting of three major parts, an electrobalance, a reactor, and a gas-delivery system, was used in this work. 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 I.D. 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 dia. ceramic tubing and positioned adjacent to the sample within the reactor. A sample tray made of alumina, 2.6 cm I.D. and 0.4 cm depth, was suspended into the uniform temperature zone of the reactor with a platinum wire.

Sample preparation

The Chevron ICE-B-GON Deicer used as the CMA sample for this study was of 96% purity, the rest being mostly inert silicate impurities. The atomic ratio of Ca to Mg in the CMA sample was determined using direct current plasma (DCP) to be 0.3 ± 0.03 to 0.7 ± 0.05. The chemical composition of CMA was, thus, confirmed to be $Ca_{0.3}Mg_{0.7}(CH_3COO)_2$. The samples were ground with a pestle and mortar to $-325+400$ mesh size (average particle size: 41 μm).

Elimination of the effects of external mass transfer and interstitial diffusion

In the measurement of the intrinsic decomposition kinetics, external mass-transfer and diffusional effects were eliminated by using a sufficiently high gas-flow rate and a sufficiently thin layer of the sample. The experiments were carried out nonisothermally under a pure nitrogen atmosphere with a flow rate of 1.81 NL/min, which was sufficient to eliminate the external mass-transfer effect (Han, 1998). A 300 mg sample of CMA powder was spread as a thin layer in the shallow sample tray, which eliminated any effect of interstitial diffusion.

Decomposition Steps and Product Morphology

Figure 1 shows a typical pattern of the decomposition of CMA. This curve has a characteristic shape that is virtually identical for all experiments performed in this work. As shown in the figure, the decomposition of CMA consisted of

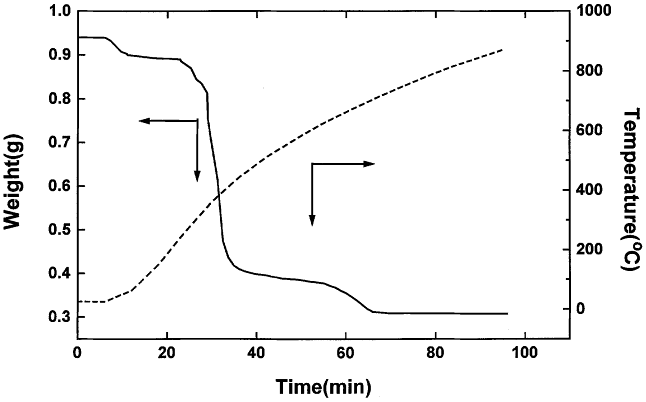

Figure 1. Typical decomposition pattern of CMA under a nonisothermal condition.

Table 1. Weights of Equivalent Components in the Starting CMA and Theoretical Weight Changes for Decomposition Reactions (1 g of CMA)

Component	Molec. Wt.	Wt. of Equiv. Comp. in Starting CMA (g/g CMA)	Theor. Wt. Loss for Stated Decomp. React. (g/g CMA)
Water (Free & Hydration)	18	0.05	
Inert material		0.04	
$CaAc_2$	158.2	0.295	
$MgAc_2$	142.4	0.617	
$CaCO_3$	100.1	0.187	$CaAc_2$ to $CaCO_3$ 0.108
$MgCO_3$	84.3	0.366	$MgAc_2$ to $MgCO_3$ 0.251
CaO	56.0	0.105	$CaCO_3$ to CaO 0.082
MgO	40.3	0.175	$MgCO_3$ to MgO 0.191

three steps. The first mass loss takes place starting at around 65°C relatively slowly with the loss of 0.052 g/g-sample. The second mass loss starts at 275°C, and the greatest loss during the decomposition of CMA takes place at this stage with the loss of 0.55 g/g-sample. The third and final decomposition step takes place starting at 580°C, and the weight loss was 0.082 g/g-sample. The most probable phases formed during the decomposition of CMA were $CaCO_3$, $MgCO_3$, CaO, and MgO.

The theoretical weight losses accompanying decomposition reactions of the various components are shown in Table 1. The first decomposition step was due to the loss of water (free and hydration), which was measured to be 0.050 g/g-sample by separate measurement. This value matches with the value of 0.052 g/g-sample during the TGA run shown in Figure 1. The confirmation by XRD could not be made because standard XRD data of the hydrated and dried CMA were not available. However, considering the temperature range of this step and the amount of mass change, it was believed that the loss of water caused the first mass loss.

The weight loss of the 0.55 g/g-sample in the second decomposition step corresponds to the sum of the weight loss (0.108 g/g-sample) by the decomposition of calcium acetate to $CaCO_3$ and the weight loss (0.44 g/g-sample) by the conversion of magnesium acetate to MgO, as shown in Table 1. An XRD analysis just after this decomposition step confirmed that CMA decomposed directly to $CaCO_3$ and MgO during this stage (Han, 1998). $MgCO_3$ was not indicated as the intermediate phase between magnesium acetate and magnesium oxide.

In the third stage, the decomposition of $CaCO_3$ to CaO took place. The measured weight loss of the 0.082 g/g-sample agrees with the theoretical weight loss of the 0.082 g/g-sample for the conversion of $CaCO_3$ to CaO. XRD analysis supported this result, showing that the final phases after the third step are CaO + MgO (Han, 1998).

As a result of the above investigation, it was found that the CMA has three decomposition steps under a nitrogen atmosphere, which were the evaporation of water in the first step starting at 65°C, the conversion of CMA into $CaCO_3$ and MgO in the second step starting at 275°C, and the decomposition of $CaCO_3$ to CaO in the third step starting at 580°C.

When CMA decomposes to a mixture of CaO and MgO, 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 in Figure 2. 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. Calcium oxide obtained by calcining calcium acetate at 800°C has been reported to contain pores in the size range of 0.2 to 4 μm (Sasaoka et al., 1997, 1998; Wu et al., 2002). 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 such very open microstructure, the calcined CMA keeps much porosity and internal surface area during the sulfation reaction, as discussed in Part II of this series. As a result, the sulfation rate of the CaO in the calcined CMA is rapid and does not level off until complete conversion. Furthermore, the sulfation capacity of the calcined CMA is much greater than that of conventional sorbents because its sulfation reaches complete conversion and its MgO content is also sulfated at temperatures lower than about 900°C, as will be shown in Parts II and III of this series (Sohn and Han, 2002a,b).

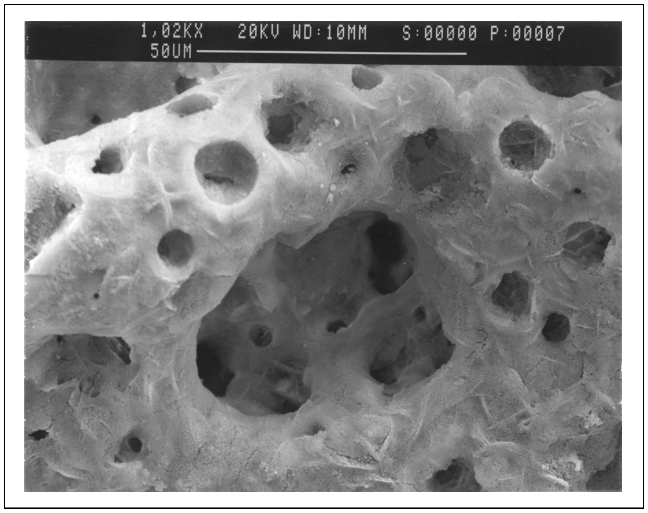

Figure 2. Scanning electron micrograph of calcined CMA.

Heating rate = 10°C/min from 275 to 1,000 °C.

Decomposition Kinetics

In this work, the intrinsic kinetics of thermal decomposition of CMA, unaffected by external mass-transfer and diffusional effects, was determined by using a sufficiently high gas-flow rate and a sufficiently thin layer of the sample, as indicated earlier.

Method of rate analysis

The kinetics of the thermal decomposition of solid-state materials often are complex (Sichen and Seetharaman, 1992; Xiao et al., 1997), and have been extensively studied (Arvanitidis et al., 1997; Bustnes et al., 1993; Dollimore et al., 1978; Dollimore and Rogers, 1979; Jagtap et al., 1992; Sharp and Wentworth, 1969). For the solid-state decomposition reaction, the following expression is typically used

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \qquad (1)$$

where α is the fractional conversion in time t, and k is the rate constant, which depends on the absolute temperature T according to the Arrhenius equation

$$k = k_o \cdot \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

From Eqs. 1 and 2

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^{t} k_o \exp\left(-\frac{E}{RT}\right) dt \tag{3}$$

The integral on the lefthand side of Eq. 3 is expressed as $g(\alpha)$, and for isothermal conditions

$$g(\alpha) = k_o \exp\left(-\frac{E}{RT}\right) t \tag{4}$$

For nonisothermal conditions, several methods have been developed to treat the conversion vs. time data (Han, 1998). For this study, the differential method was used to analyze the thermal decomposition kinetics of CMA.

From Eqs. 1 and 2

$$\frac{\frac{d\alpha}{dt}}{f(\alpha)} = k = k_o \exp\left(-\frac{E}{RT}\right) \tag{5}$$

Thus

$$\ln k = \ln\left(\frac{\frac{d\alpha}{dt}}{f(\alpha)}\right) = \ln k_o - \frac{E}{RT} \tag{6}$$

Decomposition of CMA to $CaCO_3$ + MgO

The decomposition of CMA to $CaCO_3 + MgO$ was carried out under two different heating rates, as shown in Figure 3. All data were fitted with a sixth-order polynomial function, from which $d\alpha/dt$ was calculated. The conversion α used for this study was defined as

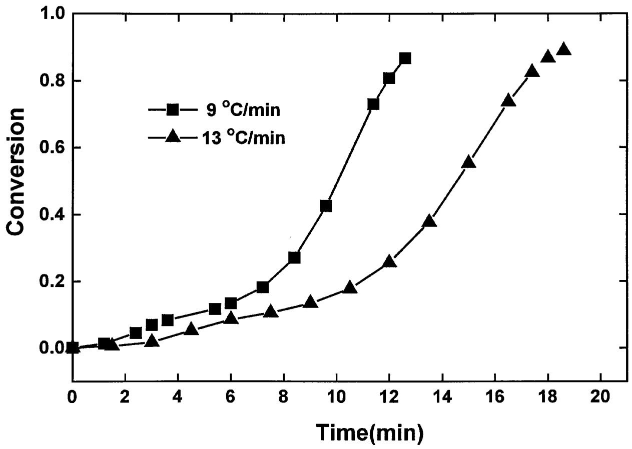

Figure 3. Polynomial fitting of data for the decomposition of CMA to $CaCO_3$ and MgO.

Temperature range = 275–580°C.

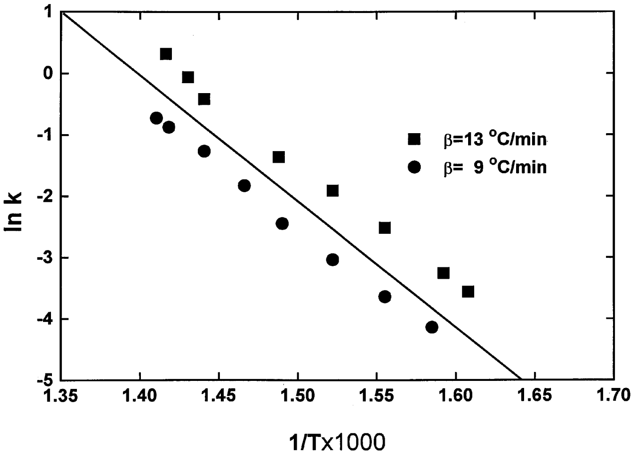

Figure 4. Result of applying the differential method to the decomposition data for dried CMA to $CaCO_3$ + MgO, according to Eq. 6.

β is the linear heating rate.

$$\alpha = \frac{\Delta W}{\Delta W_{th}} \tag{7}$$

where ΔW is the actual weight change on conversion, and ΔW_{th} is the theoretical weight change which was verified experimentally. Figure 3 shows experimental results (continuous outputs of the TGA recording balance) represented by the symbols and the polynomial-fitted continuous curves. Among the many different rate expressions tested, the pseudo-first-order kinetic equation represented by

$$f(\alpha) = (1-\alpha) \tag{8}$$

in Eq. 1 was observed to give the best straight line, as shown in Figure 4. The activation energy and the pre-exponential factor of the decomposition reaction of CMA to calcium carbonate and magnesium oxide were obtained from the slope and the intercept of Figure 4. According to Eq. 6, the kinetic parameters should be independent of the heating rate: the activation energy is the same for both heating rates, but there appears to be a moderate systematic difference in the pre-exponential factor, with the extent of the difference as given in Eq. 9. The activation energy and the average pre-exponential factor were calculated to be 165.5 kJ/mol and 1.3×10^{12} $\min^{-1}$, respectively. Therefore, the reaction rate equation for CMA to $CaCO_3$ and MgO is

$$-\ln(1-\alpha) = 1.3(\pm 0.4) \times 10^{12} \cdot \exp\left(\frac{-19{,}906}{T}\right) \cdot t \tag{9}$$

Although there appears in this case to be some effect of heating rate on the pre-exponential factor, the complete rate expression obtained in this work should be applicable to the case of other heating schedules with reasonable quantitative confidence. This is because the largest portion of the decomposition takes place in the high temperature range where the sample spends a relatively short length of time. Further, the

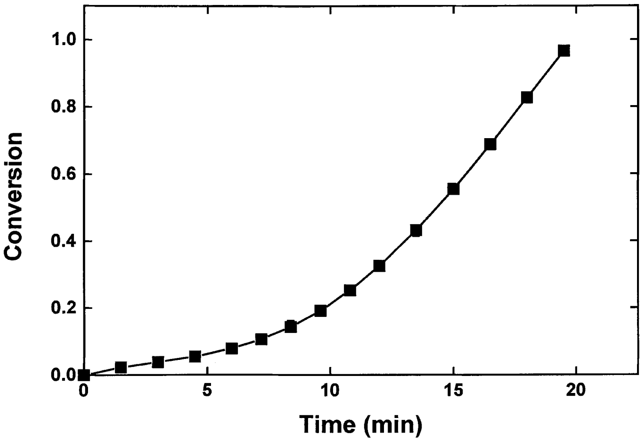

Figure 5. Polynomial fitting of data for decomposition of $CaCO_3$ to CaO.

Linear heating rate = 10°C/min; temperature range = 580–750°C.

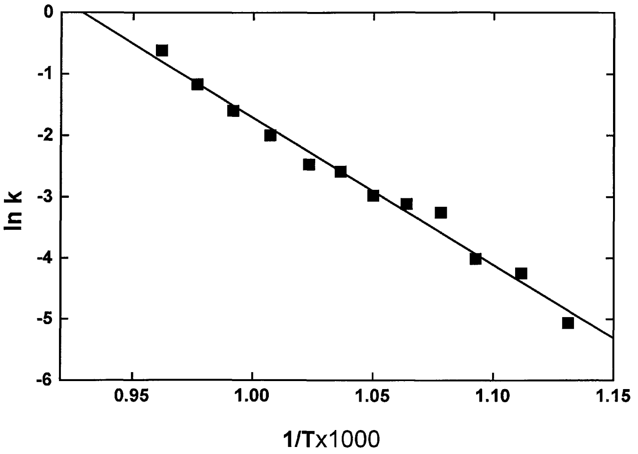

Figure 6. Result of applying the differential method to the decomposition of $CaCO_3$ to CaO, according to Eq. 6.

Linear heating rate = 10°C/min.

sulfation reactivity of the decomposition product is mainly dependent on the length of time the decomposition product is exposed to high temperatures, because sintering is highly temperature sensitive. Even at the heating rates used in this work, the samples are exposed to high temperatures for only limited lengths of time.

Decomposition of $CaCO_3$ + MgO to CaO + MgO

The next decomposition step is calcium carbonate to calcium oxide. Unlike the decomposition of CMA to $CaCO_3$ + MgO, numerous experiments for the decomposition of $CaCO_3$ to CaO have previously been carried out under various conditions. Table 2 shows a selection of literature values for the activation energy of the thermal decomposition of calcium carbonate.

This decomposition curve was fitted by a fourth-order polynomial curve to obtain $d\alpha/dt$. Figure 5 shows the polynomial curve and the TGA output obtained at 10 K/min heating rate, represented by the symbols. Again, the pseudo-first-order kinetics best matched the data for calcium carbonate decomposition. As shown in Figure 6, the activation energy and frequency factor of the decomposition of calcium carbonate originating from CMA were 6.03×10^{9} min^{-1} and 200 kJ/mol. For this decomposition reaction, the rate equation is, thus

$$-\ln(1-\alpha) = 6.03\times10^{9}\cdot\exp\left(\frac{-24{,}056}{T}\right)\cdot t \qquad (10)$$

The activation energy value had a good agreement with the values in Table 2. Figure 7 shows the conversion vs. time curves of some of the previous samples in Table 2. These curves were generated for the isothermal condition of 700°C. As shown in the figure, the decomposition rate of calcium carbonate originating from CMA to CaO is relatively fast due to its high initial porosity.

Conclusions

The first step in the possible use of CMA for a reaction with and removal of sulfur dioxide is its thermal decomposition. The decomposition reaction was determined to proceed in three steps: the evaporation of water in the first step starting at 65°C, the conversion of CMA into $CaCO_3$ and MgO in the second step starting at 275°C, and the decomposition of $CaCO_3$ to CaO in the third step starting at 580°C. The decomposition kinetics were determined nonisothermally. The pseudo-first-order kinetic equation was observed for the decomposition of CMA to $CaCO_3$ + MgO. The activation energy and pre-exponential factor were 165.5 kJ/mol and 1.3×10^{12} min^{-1}, respectively. The decomposition of $CaCO_3$ to

Table 2. Activation Energy for Decomposition of Calcium Carbonate from Previous Work

Ref.	Particle Size (μm)	Activation Energy (kJ/mol)	Atm.	Method
Guler et al. (1982)	45–53	190–220	N_2	nonisothermal
Melling et al. (1969)		184–212	N_2	nonisothermal
Reading et al. (1984)	20–44	190–209	O_2	isothermal
Gallagher and Johnson (1973)		170.5	N_2	nonisothermal
Berlin and Robinson (1962)		163.8	air	nonisothermal
Freeman and Carroll (1958)	< 56	170.5	air	isothermal
Ingraham and Marier (1963)		184.8	N_2	nonisothermal
This work	37–44	200	N_2	nonisothermal

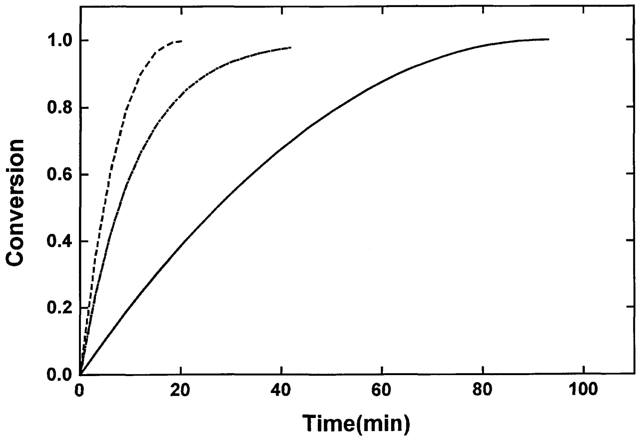

Figure 7. Conversion vs. time at 700°C for different $CaCO_3$ samples generated from the given rate equations.

—— Gallagher and Johnson (1973), particle size = 20−40 μm; – – – Ingraham and Marier (1963), particle size = < 50 μm; —·—·— this Work, particle size = 41 μm.

CaO also obeyed the pseudo-first-order kinetics with an activation energy and a pre-exponential factor of 200 kJ/mol and 6.03×10^9 min^{-1}, respectively.

The calcination product from CMA is quite reactive due to the large porosity and internal surface area generated upon the removal of the acetate group during the decomposition reaction. An example is the high decomposition reactivity of the intermediate $CaCO_3$.

Acknowledgment

The authors wish to thank Chevron for their support of this work and for providing the calcium magnesium acetate sample used in this work.

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Manuscript received Jan. 2, 2002, and revision received May 28, 2002.