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# Kinetic analysis from dilatometry and mass spectrometry measurements of the decomposition and sintering of calcium carbonate

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The decomposition and sintering of calcium carbonate were examined in a combined dilatometer and mass spectrometer apparatus. Carbon dioxide from the decomposition reaction is evolved from 600-1000°C for heating rates of 1-15 K minute<sup>-1</sup>. During the decomposition reaction, an initial period of shrinkage of 2-4% was observed. Above 1100°C, a second period of shrinkage of 2-4% occurred, which is attributed to the sintering of the calcium oxide produced from the decomposition reaction. Kinetic rate parameters for the decomposition, initial stage of shrinkage, and relative density were analyzed by reaction and sintering models using integral methods of analysis. Both the decomposition and relative density were reasonably well described with an activation energy of 115-120 kJ mol<sup>-1</sup> for the full range of conversion over a wide range of temperature. The initial stage of shrinkage was described by a diffusion mechanism with an activation energy of 225 kJ mol<sup>-1</sup>.

Key words: Calcium Carbonate, Decomposition, Sintering, Kinetic Analysis.

### Introduction

During the heating of calcium carbonate to high temperature, carbon dioxide is evolved as the carbonate decomposes. Along with this reaction, the microstructure transforms as changes occur in crystallographic phase, porosity, density, and surface area. The number of phenomena occurring and their relationship thus make calcium carbonate an interesting model system for scientific investigation. In addition to scientific interest, the decomposition and sintering of calcium carbonate has technological importance because of the use of limestone in flue-gas desulfurization, and because of the difficulty in sintering both calcium carbonate and calcium oxide to high density.

Although a large number of studies have been performed on the decomposition kinetics of calcium carbonate [1-14], consensus has not emerged on all of the mechanistic details. Most models assume, however, that the decomposition occurs as an advancing front, and the carbon dioxide generated must then diffuse through the calcium oxide product layer. Further complicating the description of the decomposition mechanism is that the effects of mass and heat transfer have been identified as influencing the apparent kinetics, and these transport limitations become especially pronounced as the particle size increases. The decomposition of calcium carbonate is also known to depend on the atmosphere, with carbon dioxide retarding the decomposition [4, 6, 11, 13].

The microstructural evolution occurring during the decomposition of calcium carbonate is complex as well [15, 16]. Calcium carbonate in the calcite phase is of rhombohedral crystal symmetry with carbonate groups located in positions halfway between calcium layers [17]. The final structure after decomposition and rearrangement to calcium oxide is the rock salt structure, which can be derived from the rhombohedral structure by replacement of carbonate groups with oxygen atoms and then compressing along the rhombohedral 3-fold axis. For this process alone, porosity is created which corresponds to 54% of the initial volume of theoretically-dense calcium carbonate. The maximum amount of linear shrinkage that can occur with the loss of this porosity is 23%. For polycrystalline samples of calcium carbonate, additional inter- and intra-particle porosity is present as well. Thus, as the crystal structure changes during decomposition, changes in the surface area, porosity, particle size, and external dimensions occur as well.

The evolution of the microstructural phenomena at high temperature are typically described in terms of sintering models. In general, for bodies consisting of packed particles with no intra-particle porosity, the surface area, number of pores, total porosity, and external dimensions decrease with sintering time whereas the density, particle (grain) size, and pore size all increase. For the case of calcium carbonate, however, such a simplified picture does not hold because both weight loss and sintering are occurring. The decomposition of calcium carbonate leads to an initially high-surface area calcium oxide with near 50% porosity [18]. With continued exposure to elevated temperature, the calcium oxide undergoes a reduction in surface area [8, 10, 16,

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18-20], which has been described by an early-stage sintering model [21]. Reduction in the microporosity (<0.19  $\mu$ m pore diameter) also occurs, which has been described by an intermediate-stage sintering model [22]. The micropore radius, on the other hand, has been shown to increase with increasing time and temperature [16]. In spite of these microstructural changes, the amount of shrinkage experienced by the samples has been reported to be negligible [6, 11] or <10% [16].

These observations on the surface area, porosity, pore radius, and external dimensions have been supported by microscopy studies of the decomposition of calcium carbonate [15, 16] and magnesium carbonate [23, 24], which is isostructural with calcium carbonate. When single crystals of magnesium carbonate are heated, the conversion to magnesium oxide is pseudomorphic, *i.e.*, no changes occur in the external shape and dimensions of the sample. The escaping carbon dioxide thus leaves behind a high-surface area pore volume, which is related to the difference in density between the two solids. Although no changes in the external dimensions of the single crystal occur during decomposition, fissures or cracks do appear, and these have been attributed to a coalescence of small crystallites so as to reduce the energy associated with the high surface area.

The evolution of the microstructure of polycrystalline calcium carbonate has been examined as well and a qualitatively similar picture holds [16]. For these samples, linear shrinkage of 10-15% was observed, but it was not possible to identify when in the process this occurred. The presence of carbon dioxide in the gas phase has been shown to enhance the sintering rates of both calcium carbonate [20, 25] and calcium oxide [5, 26].

A number of studies of calcium carbonate decomposition and calcium oxide sintering have focused on the evolution of surface area and porosity, and these are clearly important for characterizing the rate of sulfur dioxide fixation [27-29]. It is also desirable to have, however, independent measurements of the rates of decomposition, dimensional changes, and density as a function of temperature and time. One approach to accomplish this is to monitor simultaneously the gas phase with a mass spectrometer and the linear shrinkage with a dilatometer [30, 31]. We have conducted such measurements on samples of calcium carbonate and have used kinetic models for decomposition and sintering to obtain rate parameters for some the different phenomena that are occurring at high temperature.

## **Experimental**

The experiment apparatus [30, 31] consists of a gas handling system, a furnace/dilatometer unit (L70/2000, Linseis, Germany), and a mass spectrometer (Hewlett Packard 5971). The temperature of the furnace and sample is measured by a W5%-Re26% (type C) thermocouple placed directly below the sample holder. A por-

tion of the exit gas from the furnace is introduced into the mass spectrometer which has an electron multiplier detector.

To obtain the partial pressure,  $P_A$  of the parent compound A indicated by the intensity  $(I_{Ai})$  from the mass spectrometer at a mass/charge ratio m/z = i, we use [30]

$$P_{A} = \frac{I_{Ai}}{\Gamma_{Ai}} \frac{\Gamma_{N_{2}}}{\Omega_{A} T F_{i} D F_{i} S}$$
(1)

where  $\Gamma_{N_2}$  is the fragmentation factor for N<sub>2</sub><sup>+</sup> ions,  $\Gamma_{Ai}$ , is the fragmentation factor for species *i* of parent compound *A*,  $\Omega_A$  is the ionization probability of species *A*, *TF<sub>i</sub>* is the transmission factor of species *i*, equal to 28/*M* (where *M* is the molecular weight), *DF<sub>i</sub>* is the detection factor of species *i*, taken as unity, and *S* is the sensitivity for nitrogen. Values for some of these quantities for the species under investigation here are listed in Table 1.

The conversion of calcium carbonate,  $\alpha$ , as a function of time can then be obtained by integrating the area under the intensity curves as

$$\alpha = \frac{1}{A_t} \int_0^t I dt \tag{2}$$

where  $A_t$  is the total integrated area. Equation (2) can thus be used to convert gas-phase intensity data into conversion or weight loss profiles similar to what is obtained from thermogravimetric experiments.

For each experiment, the furnace is first evacuated to 50 millitorr at room temperature and then backfilled with Ar (purity  $\geq$  99.99%). The furnace is heated under vacuum to 200°C and then held for 20 minutes to remove gases weakly adsorbed by the graphite elements and insulation. Argon is then introduced into the furnace

Table 1. Ionization probability and fragmentation factor for selected species. The sensitivity of mass spectrometer to nitrogen is S=2800/mtorr

Species	m/z	Relative Ionization Sensitivity, $\Omega$	Fragmentation Factor, Γ
СО	28	1.05	0.930
	16	_	0.029
	12	_	0.036
$CO_2$	44	1.4	0.853
	28	_	0.069
	16	-	0.057
	12	-	0.021
Ar	40	1.2	0.945
	20	_	0.055
$O_2$	32	1.0	0.731
	16	_	0.269
$N_2$	28	1.0	0.855
	14	_	0.145

at 16 liter  $h^{-1}$  and 1 atm total pressure. The sample shrinkage and gas-phase composition are then monitored as a function of temperature.

The sample for each run is 0.7 g of CaCO<sub>3</sub> powder (purity >99.95%, Sigma-Aldrich, Milwaukee, WI) with 1% by weight binder (D3005, Rohm and Hass, Philadelphia, PA). The powder is pressed into a cylindrical shape of 1 cm height by 0.6 cm diameter.

## **Results and Discussion**

For the first experiment, a specimen of calcium carbonate was heated in flowing argon at  $\beta=5$  K minute<sup>-1</sup> followed by a 60 minute hold at 1200°C. The intensities of the species for m/z=28 and 44 observed in the gas phase as a function of temperature are shown in Fig. 1 along with the shrinkage of the sample. Over the temperature range of  $T=550-1000^{\circ}$ C, CO<sub>2</sub> (m/ z=44) is evolved and has a maximum intensity near  $T=850^{\circ}$ C, which corresponds to a pressure of 37 torr in the furnace effluent. The intensities of CO, (m/z=28)and the fragments m/z=12 (C), 16 (O), not shown here) as a function of temperature are similar in shape to that of the CO<sub>2</sub> signal, and these masses appear in concentrations consistent with the fragmentation factors for CO<sub>2</sub> listed in Table 1. Above 900°C, the intensity of m/z=44 continues to decrease whereas a second smaller maximum occurs in the m/z=28 signal at  $T=950^{\circ}$ C. The appearance of the second m/z=28 peak arises from the reaction of  $CO_2$  with the graphite in the furnace, and this has been verified [30] by solving for the equilibrium concentrations for mixtures of CO<sub>2</sub>, C, and CO as a function of temperature.

The dimensional change of the sample as a function of temperature is also displayed in Fig. 1. In the initial part of the cycle to 600°C, the sample expands by approximately 0.5%, and this is consistent with the tabulated coefficient of thermal expansion (CTE) value



**Fig. 1.** Intensity of carbon dioxide (m/z=44) and carbon monoxide (m/z=28) and dimensional change versus temperature. The sample of calcium carbonate was heated in flowing argon at 5 K minute<sup>-1</sup> to 1200°C followed by a 1 h hold.

for calcium carbonate [32]. Above 600°C, two regions of shrinkage of the sample are observed. The first period of shrinkage occurs over the same range of temperature corresponding to the evolution of  $CO_2$ , and the sample continues to shrink until 900°C when the evolution of  $CO_2$  stops as the decomposition reaction goes to completion. From 900-1100°C, the sample expands by 0.2%, which is much less than the tabulated amount for calcium oxide [32]. This small amount of expansion arises because sintering and expansion of the sample are competing phenomena. Above 1100°C, the sample resumes shrinking as the calcium oxide sinters.

The mass intensity data for  $CO_2$  in Fig. 1 can be converted into units of normalized weight loss or conversion by integrating the m/z=44 signal with Eqs. (1) and (2) to determine the moles of  $CO_2$  produced by decomposition. In general, the weight loss calculated from the integrated intensity signals is within ±10% of the gravimetric and stoichiometric amounts [31]. The conversion profiles of CaCO<sub>3</sub> as a function of the heating rate are shown in Fig. 2a. The conversion occurs at progressively higher temperatures with increasing heating rate, and the profiles all appear similar, which sug-



**Fig. 2.** (a) Normalized weight of calcium carbonate as a function of temperature at different heating rates. (b) Dimensional change of calcium carbonate sample as a function of temperature at different heating rates.

Heating rate, $\beta$ (K minute <sup>-1</sup> )	First Shrinkage (%)	Second Shrinkage (%)	Total Shrinkage (%)
1	2.0	1.9	3.91
5	2.6	1.4	3.96
10	2.7	1.7	4.41
15	3.5	2.1	5.64

**Table 2.** Dimensional changes for calcium carbonate samples as a function of heating rate to 1200°C followed by a 1 h hold

gests that a common kinetic mechanism underlies the decomposition. These data also indicate that conversion versus temperature span a relatively large temperature range of 600°C, as compared to the temperature range when only a single heating rate is employed.

The shrinkage of the CaCO<sub>3</sub> as a function of heating rate is displayed in Fig. 2b. For all of the heating rates, the decomposition and initial period of shrinkage both occur over the same temperature range. For heating rates of 5, 10, and 15 K minute<sup>-1</sup>, the first 3% of shrinkage are nearly superimposed, in contrast to the 1 K minute<sup>-1</sup> shrinkage data. At the faster heating rates, a diffusional step underlying the microstructural rearrangement may be rate-limiting.

Over the temperature range corresponding to the decomposition, the amount of initial shrinkage is proportional to the heating rate (see Table 2), as is the total amount of shrinkage. This arises because with higher heating rates, the decomposition reaction occurs over a smaller time span and thus the concentration of  $CO_2$  in the gas phase is greater. This is consistent with the reported catalytic effect of  $CO_2$  on the sintering of  $CaCO_3$  [20, 25] and CaO [5, 26].

Because the samples shrink, the decomposition of calcium carbonate is not pseudomorphic. This may arise because the samples examined here are pressed compacts of particles that can deform relatively easily when a stress is present. Some of the shrinkage arises from atomic rearrangement between the two crystal structures while the balance corresponds to sintering of the sample. Based on the unit cell dimensions of CaCO<sub>3</sub> and CaO, an average linear shrinkage of 23% may be expected in transforming from the starting to the final crystal structure. For complete transformation and no shrinkage, porosity of 54% must be present in the body. For the pressed compacts used here of 33 volume%

initial porosity, a maximum shrinkage of 32% is possible. The total observed shrinkage here of only 6% is consistent with the known difficulty in sintering CaO without sintering aids [5, 16]. The total shrinkage of 6% thus corresponds to porosity of roughly 67 volume%, which is consistent with the very friable physical texture of the samples after heating.

The decomposition data in Fig. 2 were analyzed by integral kinetic methods [33, 34] to obtain the preexponential factor, *A*, and the activation energy, *E*. For a kinetic process that depends on some function,  $f(\alpha)$ , where  $\alpha$  is the fraction of decomposed material, the rate expression for a thermally activated process can be expressed as

$$\frac{d\alpha}{dt} = A \exp\left[\frac{-E}{RT}\right] f(\alpha) \tag{3}$$

where *R* is the gas constant. For experiments conducted with a constant heating rate,  $\beta$ , the activation energy and pre-exponential factor can be determined from [35]:

$$\ln\left[\frac{F(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta(E+2RT)}\right] - \frac{E}{RT}$$
(4)

where  $F(\alpha)$  is obtained from

$$F(\alpha) = \int \frac{d\alpha}{f(\alpha)}$$
(5)

The different forms of  $f(\alpha)$  and  $F(\alpha)$  are summarized in Table 3 for models for first-order, diffusion control, and surface-reaction control. For the first-order case, the effect of the CO<sub>2</sub> partial pressure is neglected, because it is always small under the conditions of dynamic purge used here. From inspection of the forms of  $f(\alpha)$ and  $F(\alpha)$  in Table 3, we can expect that the profiles of  $f(\alpha)$  for the individual mechanisms will be different as a function of conversion.

Table 4 summarizes the activation energies and preexponential factors obtained for the different kinetic mechanisms at each heating rate. The values of A and E span a wide range and depend on the mechanism assumed and on the heating rate. For each mechanism, analysis of conversion data obtained at the heating rates of 5, 10, and 15 K minute<sup>-1</sup> leads to values of A and Ethat span a narrow range of values; data obtained at 1 K

 Table 3. Kinetic models used to analyze the decomposition of calcium carbonate

Kinetic Models		$f(\alpha)$	$F(\alpha)$
First Order		1-α	$-\ln(1-\alpha)$
Diffusion Control	Parabolic Law Jander Equation Valensi Equation	$\frac{\alpha^{-1}}{3(1-\alpha)^{1/3}/[2(1-\alpha)^{-1/3}-2]}$ [-ln(1-\alpha)] <sup>-1</sup>	$\frac{\alpha^{2}/2}{[1-(1-\alpha)^{1/3}]^{2}}$ (1-\alpha)ln(1-\alpha)+\alpha
Surface Reaction Contr	rol	$3(1-\alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$

Madal	β	А	Е	$r^2$	α	Temperature Range,
Model	(K minute <sup>-1</sup> )	$(s^{-1})$	$(kJ mol^{-1})$	(-)	(-)	(°C)
First-Order	1	$1.55 \times 10^{4}$	150	0.99	0.002-0.99	510-860
	5	267	115	0.99	0.02-0.99	600-990
	10	87	106	0.99	0.02-0.97	610-1070
	15	144	112	0.99	0.08-0.95	590-1010
Surface Reaction Control	1	2935	146	0.99	0.002-0.95	510-800
	5	7	96	0.99	0.02-0.88	580-890
	10	11	99	0.99	0.02-0.88	590-970
	15	38	111	0.99	0.01-0.88	620-1020
Diffusion: Parabolic Law	1	2.61×10 <sup>11</sup>	295	0.99	0.02-0.77	510-760
	5	$4.43 \times 10^{6}$	214	0.99	0.08-0.82	580-890
	10	$2.08 \times 10^{5}$	193	0.99	0.02-0.88	590-970
	15	$1.72 \times 10^{6}$	218	0.99	0.01-0.88	620-1020
Diffusion: Valensi	1	8.32×10 <sup>11</sup>	303	0.99	0.002-0.77	510-760
Equation	5	$6.08 \times 10^{6}$	215	0.99	0.01-0.88	620-1020
	10	7.93×10 <sup>5</sup>	203	0.99	0.02-0.88	590-970
	15	$6.28 \times 10^{6}$	228	0.99	0.01-0.88	620-1020
Diffusion: Jander Equation	1	$6.67 \times 10^{11}$	312	0.99	0.02-0.77	510-760
	5	$7.61 \times 10^{6}$	228	0.99	0.01-0.88	620-1020
	10	8.53×10 <sup>5</sup>	215	0.99	0.02-0.88	590-970
	15	6.43×10 <sup>6</sup>	240	0.99	0.01-0.88	620-1020

Table 4. Activation energies and pre-exponential factors for calcium carbonate decomposition as a function of linear heating rate and kinetic model

minute<sup>-1</sup> leads to higher values of *A* and *E*. All of the diffusion models lead to values of the activation energy that are almost a factor of two larger than the values obtained from the first-order and surface-reaction controlled models. A compensation effect [33, 36] between *A* and *E* is also evident in that larger values of *E* coincide with larger values of *A*.

For the integral method given by Eq. (4), a linear region between  $\ln(F(\alpha)/T^2)$  and 1/T is obtained in the analysis, and the regression coefficients,  $r^2$ , for the range of  $\alpha$  are all 0.99 or greater (see Table 4). For the first order method, approximately 90-95% of the conversion data falls in the linear region. For the surface-reaction and diffusion-controlled mechanisms, 80-90% of the conversion exhibits the linear behavior suggested by the underlying model.

The kinetic parameters in Table 4 were used with a finite difference model to simulate the observed decomposition kinetics for a heating rate of 5 K minute<sup>-1</sup>. Figure 3 indicates that with the exception of the surface reaction control model, the other mechanisms provide an adequate description of the kinetics over the range of conversion from 0-70%. Above 80% conversion, the first-order and Jander diffusion mechanisms best describe the sigmoid tail observed in the experiments, whereas the Valensi and parabolic diffusion models are less satisfactory.

The values of  $A=270 \text{ s}^{-1}$  and  $E=115 \text{ kJ mol}^{-1}$  obtained at 5 K minute<sup>-1</sup> from the first-order mechanism were also used to simulate the experimental data obtained at the other heating rates. Figure 4 illustrates that when



**Fig. 3.** Simulated weight loss profiles with temperature for firstorder, diffusion- and surface-reaction controlled mechanisms as compared to the data obtained in the experiments at a heating rate of 5 K minute<sup>-1</sup>.

this is done, the level of model prediction becomes less satisfactory for the heating rates farthest removed from 5 K minute<sup>-1</sup>. Much less satisfactory agreement was obtained when the kinetic parameters for the Jander diffusion- and surface reaction-controlled mechanisms were used at the other heating rates.

The values for the activation energy in Table 4 fall within the wide range reported in the literature [1-14, 33], but more importantly, they indicate how the assumption of a model leads to widely differing sets of kinetic parameters. Only in trying to simulate other



**Fig. 4.** Comparison of the simulated kinetics (dashed lines) and experimental data at different heating rates. All of the simulations were conducted with the same values  $A=276 \text{ s}^{-1}$  and  $E=115 \text{ kJ} \text{ mol}^{-1}$  obtained from a first-order model for experimental data (solid lines) recorded at 5 K minute<sup>-1</sup>.

experimental data does the usefulness of the kinetic parameters become apparent. The fact that apparent first-order kinetics may describe kinetic data for which the believed underlying mechanism is not purely first order has been observed elsewhere as well [33].

The shrinkage data in Fig. 3 were analyzed by the Master Sintering Curve (MSC) methodology [37] to obtain the activation energy of the underlying mass transport process. To use this method, the relative shrinkage or relative density of the sample is plotted versus the logarithm of the function  $\Theta[t,T(t)]$ :

$$\Theta[t,T(t)] \equiv \int_{0}^{t} \frac{1}{T} \exp\left(-\frac{E}{RT}\right) dt$$
(6)

For the correct value for E, the shrinkage or relative density data obtained at different heating rates superimpose onto a common curve, which is termed the MSC.

Figure 5 illustrates this methodology for the initial stage of shrinkage shown in Fig. 2b. For an activation energy of 225 kJ mol<sup>-1</sup>, which was obtained by least squares minimization, the shrinkage data obtained at the four heating rates superimpose onto a common curve. This value is very different from the activation energy of 115 kJ mol<sup>-1</sup> that describes the decomposition kinetics over the widest range of conversion. The difference between these two values of the activation energy suggests that the pathways by which decomposition and shrinkage occur have different energetic barriers. The activation energy of 225 kJ mol<sup>-1</sup> is also much higher than the activation energy of approximately 120 kJ mol<sup>-1</sup> [8] associated with the reduction in surface area. This is consistent with the idea that internally, a relatively facile change in the surface area is occurring that is not directly manifested in a change



**Fig. 5.** Initial stage of dimensional change for the decomposition of calcium carbonate as a function of  $\log[\Theta(t, T(t))]$  at different heating rates. The Master Sintering Curve method was used to determine the best-fit value of E=225 kJ mol<sup>-1</sup>.

in the external dimensions of the sample.

When  $CaCO_3$  is heated to high temperature, the bulk density is changing due to weight loss, crystallographic transformation between the calcite and rock salt structures, porosity generation, and bulk-like sintering. To describe the combined effects of these phenomena, we define the bulk density for a two-phase mixture as

$$\rho(t,T) = \frac{m_{CC} + m_{CaO}}{V_t} \tag{7}$$

where *m* denotes the mass of calcium carbonate (CC) and calcium oxide (CaO). The two masses at any point in the heating cycle can be obtained from the integrated mass spectrometer intensity data. The total volume,  $V_t$ , of the sample is also time dependent and can be obtained from the dilatometer curves along with the known initial volume.

A relative density throughout the heating cycle can then be obtained by normalizing the density in Eq. (7) by the theoretical density of mixtures of calcium carbonate and calcium oxide:

$$\rho_{th}(t,T) = \frac{m_{CC} + m_{CaO}}{\frac{m_{CC}}{\rho_{th,CC}} + \frac{m_{CaO}}{\rho_{th,CaO}}}$$
(8)

where  $\rho_{th}$  denotes the theoretical density. The relative density profiles as a function of temperature and heating rate are illustrated in Fig. 6, where it can be seen that treating the weight loss and shrinkage data in this fashion leads to smooth profiles with some similarity in shape to the conversion versus temperature profiles in Fig. 2a. Although the total shrinkage of the samples is only 4-6%, the relative density changes by nearly a factor of one-third during the heating cycle, mainly as a consequence of the weight loss.



**Fig. 6.** Relative density versus temperature for the decomposition of calcium carbonate at different heating rates. The relative density was calculated by taking into account both the weight loss and dimensional change of the sample.



**Fig. 7.** Relative density as a function of  $\log[\Theta(t, T(t))]$  for the decomposition of calcium carbonate at different heating rates. The Master Sintering Curve method was used to determine the best-fit value of E=120 kJ mol<sup>-1</sup>.

The relative density data in Fig. 6 can also be analyzed by the MSC approach to obtain an apparent activation energy. Figure 7 illustrates the superposition of the relative density profiles as a function of  $\Theta[t,T(t)]$  for E=120 kJ mol<sup>-1</sup>. This value, which is very close to the activation energy obtained from the decomposition data analyzed by a first-order mechanism, arises because the relative density, as defined in Eq. (8), depends strongly on the amount of weight loss experienced by the sample, and the first-order mechanism best describes this over the largest range of conversion. Use of an activation energy corresponding to the diffusion- or reaction-controlled mechanisms leads to much poorer superposition of the relative density curves.

The kinetic analyses used here thus provide a means for describing decomposition and dimensional changes as a function of temperature and conversion. For the decomposition of calcium carbonate, the kinetics can be reasonably well described by an apparent first-order kinetic model with  $A=267 \text{ s}^{-1}$  and  $E=115 \text{ kJ mol}^{-1}$ . The shrinkage of the sample accompanying the decomposition is best described by an activation energy of 225 kJ mol<sup>-1</sup>. When the effects of decomposition and shrinkage are combined in the relative density as given by Eq. (8), a value of  $E=120 \text{ kJ mol}^{-1}$  can be used to describe the relative density as a function of time and temperature. Although the parameters proposhere do not provide perfect agreement, they do provide reasonable values over a 600°C temperature range which are within 20% accuracy for conversion and 10% for the relative density.

## Conclusions

A combined mass spectrometer and dilatometer system has been used to examine the decomposition and sintering of calcium carbonate. The calcium carbonate decomposes over a 300-600°C temperature range, which depends on the heating rate. The sample shrinkage occurred over two distinct temperature intervals. The first period of shrinkage is correlated to the evolution of carbon dioxide from the decomposition reaction, and the second period of shrinkage was ascribed to calcium oxide sintering. Models for the kinetics of decomposition and for the first stage of shrinkage were utilized to extract the rate parameters. Both the rate of decomposition and the relative density were reasonably well-described with activation energies of 115 and 120 kJ mol<sup>-1</sup>, respectively, whereas the first stage of shrinkage was described by an activation energy of 225 kJ mol<sup>-1</sup>.

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