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Sulfation of dolomite particles at high CO_2 partial pressures

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Abstract

The sulfation reaction of half-calcined dolomite particles at high CO_2 partial pressures (around 1 bar) was investigated. The experiments were carried out in two different reactors: (a) a thermogravimetric analysis system (slow heating rates) and (b) a shock-microreactor (rapid heating rates). The experiments were carried out under isothermal conditions at temperatures between 650 and 875°C. A natural dolomite sample was used. Different particle sizes were tested: 26, 128, 256 and 512 μm. Under reaction conditions employed in the experiments ($P_{CO_2} \approx 1$ atm and $T < 900°C$), half-calcination of dolomite particles takes place and the sulfation reaction occurs between $CaCO_3 \cdot MgO$ and SO_2. The $CaCO_3$ is the only active species during sulfation. The particle size and temperature have a strong influence on the variation in extent of conversion with time. Two different stages can be distinguished in the sulfation of half-calcined dolomite particles; chemical control at the onset of reaction and diffusional control at longer reaction times. When the sulfation reaction is carried out under conditions similar to those existing in a boiler (high heating rates and simultaneous calcination and sulfation), the measured reaction rates are higher than those observed from thermogravimetric experiments. At $X = 0.1$ an activation energy of 34 kcal mol^{-1} (142 kJ mol^{-1}) was measured. This value suggests that the process is controlled by a solid state diffusion mechanism.

Keywords: Carbon dioxide; Dolomite; High partial pressure; Sulphation

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1. Introduction

The utilization of limestone particles ($CaCO_3$) to retain sulfur emissions during coal combustion has been widely studied [1–5]. However, in spite of dolomite being presented as a good agent for SO_2 retention, studies on desulfuration with this material are comparatively scarce [6,7].

Previous studies [8] have highlighted differences in the textural development of calcined dolomite and limestone particles. Thus, the calcination conditions (temperature, CO_2 partial pressure, retention time) have a strong effect on the textural evolution of calcined limestone particles, but not of dolomite particles. This indicates that, in contrast to calcined limestone particles, calcined dolomite particles hardly undergo any sintering. Differences in the evolution of textural properties will lead to a distinct behavior during the sulfation reaction. Thus, the importance of the textural characteristics of calcined particles on sulfation is well established. In this sense, it is accepted that the sulfation reaction of calcined limestone particles stops as a consequence of the plugging of external pores. Therefore, the conclusions deduced from the experiments with limestone particles are not valid for dolomite particles.

The MgO formed from the calcination of dolomite is inert to the sulfation reaction. In consequence, the calcined dolomite particles have a higher pore volume (evaluated per mol of calcium) than that of limestone particles. This allows the theoretical maximum conversion attainable during sulfation (X_m) to be greater in the case of dolomite. This is demonstrated by X_m theoretical values estimated by Rubiera et al. [8], which were 49% for limestone particles and 93% for dolomite particles. Additionally, the higher pore volume will facilitate the intraparticle diffusion of the gaseous reactants. These facts suggest that dolomite is, with respect to limestone, a better desulfurant agent.

In pressurized fluidized combustors (CO_2 partial pressure around 1 atm and temperatures below 900°C), calcium carbonate decomposition is thermodynamically unfavorable. Hence, in these circumstances, the sulfation reaction will take place according to

$$CaCO_3 + SO_2 + 0.5O_2 \rightarrow CaSO_4 + CO_2 \quad (1)$$

Different studies referring to direct sulfation of limestone particles can be found in the literature [9–12]. Under the conditions used in these studies ($T < 900°C$ and $P_{CO_2} \approx 1$ atm), the reactions involved in sulfur removal by dolomite are

$$CaMg(CO_3)_2 \rightarrow CaCO_3 \cdot MgO + CO_2 \quad \text{Half-calcination} \quad (2)$$

and

$$CaCO_3 \cdot MgO + SO_2 + 0.5O_2 \rightarrow CaSO_4 \cdot MgO + CO_2 \quad \text{Sulfation} \quad (3)$$

The half-calcined dolomite ($CaCO_3 \cdot MgO$) exhibits higher porosity than uncalcined limestone. In consequence, it can be expected that the rates of sulfation reaction of half-calcined dolomite at high CO_2 partial pressures will be very different to those measured for limestone. In spite of these expected differences, there is hardly any information in the literature about the kinetics of reaction (3). Only Siegel et al. [6], Ulerich et al. [7] and Iisa and Hupa [13] have reported rate data on reaction (3).

In this study, measurements of the direct sulfation reaction rate of dolomite particles at a high CO_2 partial pressure are reported. The temperatures used are below 900°C, and the concentrations of O_2, CO_2 and SO_2 are typical for fluidized bed combustors. Additionally, the influence of the sulfation method on reactivity was tested. Analysis of the reaction rate data obtained in a shock-microreactor (SR) (high heating rates) and in a thermogravimetric apparatus (TGA) (low heating rates) are presented and discussed.

2. Experimental

The experiments were performed using raw dolomite with a composition of 58.7% $CaCO_3$, 40.0% $MgCO_3$, 0.2% SiO_2, 0.14% Al_2O_3, 0.08% TiO_2, 0.45% Fe_2O_3, 0.02% Na_2O, 0.02% K_2O and other impurities. Dolomite particles with size ranges of 20–32 μm ($d_p = 26$ μm), 106–150 μm ($d_p = 128$ μm), 212–300 μm ($d_p = 256$ μm) and 425–600 μm ($d_p = 512$ μm) were used in this study. The BET surface area of half-calcined dolomite samples (prepared in CO_2 at 850°C) was measured in nitrogen at −196°C. The obtained values were 5.36 $m^2\ g^{-1}$ ($d_p = 26$ μm) and 5.03 $m^2\ g^{-1}$ ($d_p = 128$ μm).

TGA was performed in a Setaram TAG 24 apparatus at atmospheric pressure. To minimize the resistance of mass transfer into the sample holder, a monolayer of dolomite particles was carefully spread on the platinum pan. The sample weight was dependent on particle size (i.e. for $d_p < 200$ μm the weight was under 5 mg). To avoid the loss of small solid fragments during the heating of dolomite particles (decrepitation phenomenon), a piece of quartz wool was placed over the particle layer. The procedure consisted of heating a sample at 50°C min^{-1} up to the desired temperature in a CO_2 atmosphere. When isothermal conditions were reached, a gas stream of 100 ml min^{-1} with a composition of 2600 ppm SO_2, 3.6% O_2 and CO_2 at atmospheric pressure was added. Some experiments were carried out to analyze the reaction between calcined dolomite particles and SO_2, resulting in a gas composition of 2600 ppm SO_2, 3.6% O_2 and N_2. In Fig. 1 the weight and temperature modifications during a typical experiment carried out in the thermogravimetric system are illustrated.

The SR consisted of a quartz reactor (20 mm ID) with a sintered glass plate. The reactor was placed vertically in a furnace. A gas stream with a composition of 2500 ppm SO_2, 3% O_2 and CO_2, and a flow rate of 1.5 l min^{-1} (STP) was introduced downwards through the reactor. A sample of dolomite of around 50 mg was suddenly introduced into the reactor. As a consequence of the sulfation reaction, the SO_2 concentration decreased rapidly to a minimum value and then slowly returned to the initial value. This variation was continuously monitored with an IR Beckman 880 analyzer. In Fig. 2 the typical variation in the amount of SO_2 during a sulfation experiment is shown. The extent of conversion of $CaCO_3$/CaO to $CaSO_4$

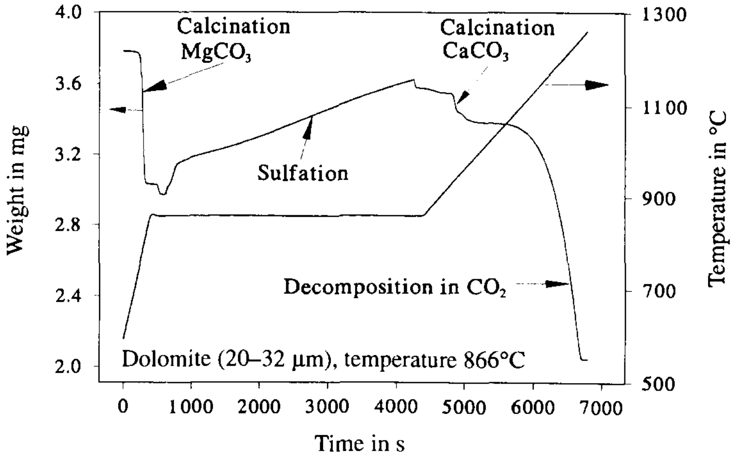

Fig. 1. Typical TG diagram for the sulfation of dolomite particles in a TGA system.

(X) and the reactivity ($\mathrm{d}X/\mathrm{d}t$) were evaluated from the breakthrough curve of SO_2 according to the following equations:

$$X = \frac{F_0}{n_0} \int_0^t (Y_0 - Y)\,\mathrm{d}t \tag{4}$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{F_0}{n_0}(Y_0 - Y) \tag{5}$$

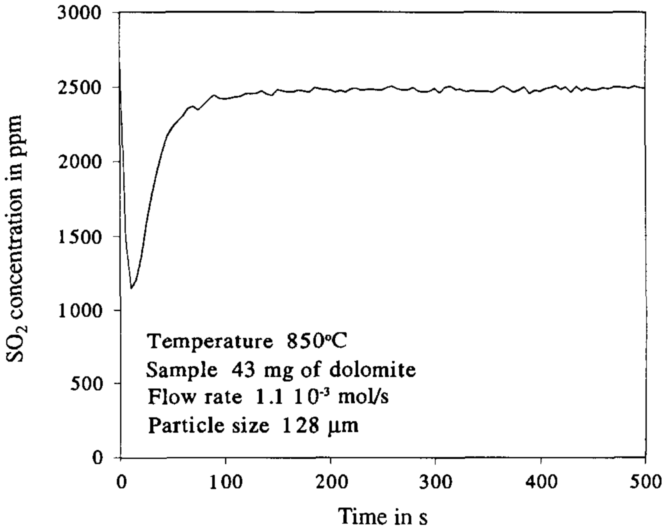

Fig. 2. Variation in SO_2 concentration during a sulfation experiment in a shock-microreactor.

where F_0 is the gas flow rate (mol s^{-1}), n_0 is the mass of the sample (mol Ca), and Y_0 and Y are the SO_2 concentrations (in mol fraction) at times $t = 0$ and t respectively.

3. Decomposition of dolomite, equilibrium calculations

The dolomite is a double carbonate of calcium and magnesium [$CaMg(CO_3)_2$]. In principle, dolomite decomposition can be studied by assuming that it is formed by $CaCO_3$ and $MgCO_3$. Erdös [14] deduced an expression for the dependence of the dissociation CO_2 partial pressure of magnesium carbonate on temperature (1 atm is 1.013 bar).

$$p_{CO_2}/(\text{atm}) = 1.339 \times 10^9\,e^{-14145/T\,(K)} \tag{6}$$

However, Baker [15] obtained the following equation for the equilibrium CO_2 partial pressure of calcium carbonate decomposition:

$$p_{CO_2}(\text{atm}) = 1.20 \times 10^7\,e^{-19130/T\,(K)} \tag{7}$$

In Fig. 3, the variations in CO_2 equilibrium partial pressure with temperature for $CaCO_3$ and $MgCO_3$ decompositions are represented. In the same Figure the operational regions (temperature and CO_2 partial pressure ranges) for different types of combustors are also indicated. For dolomite particles injected into atmospheric fluidized bed combustors (AFBC) or pulverized coal combustors (PC)

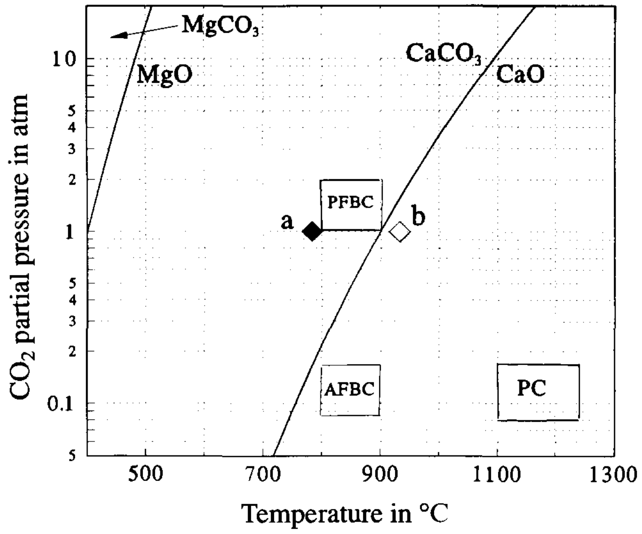

Fig. 3. Computed CO_2 equilibrium pressures of calcium carbonate (Eq. 7) and magnesium carbonate (Eq. 6) decomposition. (a) First peak of dolomite decomposition (Fig. 4); (b) second peak of dolomite decomposition (Fig. 4).

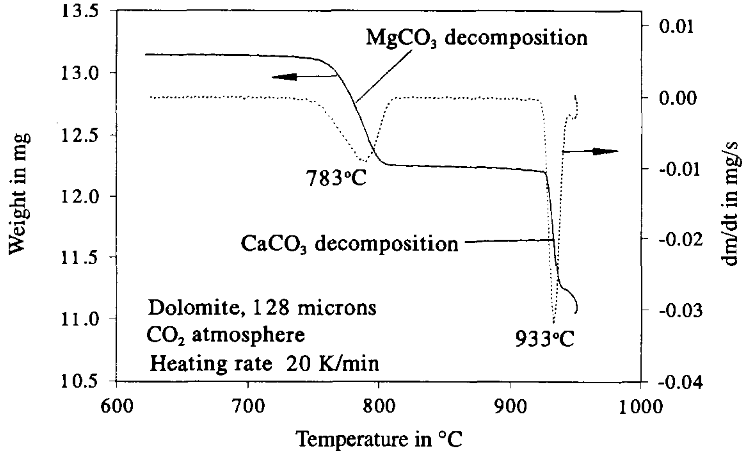

Fig. 4. TG and DTG curves for dolomite decomposition (heating rate 20 K min^{-1}; CO$_2$ atmosphere).

operating at CO$_2$ partial pressures around 0.1–0.2 atm, both MgCO$_3$ and CaCO$_3$ decompose. In pressurized systems operating at temperatures below 900°C (i.e. pressurized fluidized bed combustor (PFBC)), in which the CO$_2$ partial pressure is around 1–2 atm, MgCO$_3$ decomposes but CaCO$_3$ does not.

The decomposition of dolomite particles was investigated by heating (20 K min^{-1} in CO$_2$ atmosphere) a dolomite sample in a thermogravimetric analyzer. The obtained TG and DTG curves are shown in Fig. 4. Two DTG peaks corresponding to the CO$_2$ losses associated to magnesium and calcium respectively can be observed. The measured decomposition temperatures from the maximum DTG peaks are higher than the decomposition temperature (DT) estimated from Eqs. (7) and (8) at $p_{CO_2} = 1$ atm. Thus, at $p_{CO_2} = 1$ atm, DT = 400°C for MgCO$_3$, whereas for the first DTG peak the maximum is 783°C. For the second DTG peak, the maximum is 933°C, which is close to the estimated value for CaCO$_3$ decomposition at $p_{CO_2} = 1$ atm (900°C). These values are represented in the equilibrium diagram of MgCO$_3$–MgO–CaCO$_3$–CaO (Fig. 3). Similar results have been detected by other authors [16,17]. Thus, McIntosh et al. [16] observed, during the decomposition of dolomite particles in CO$_2$ atmosphere, two DTG peaks at 790°C and 955°C (heating rate: 7 K min^{-1}). According to these authors, the peak temperature of the first stage of the decomposition corresponds to the dissociation of dolomite into the two separate carbonates, and is not related to the thermodynamic of MgCO$_3$ decomposition. Thus

$$CaMg(CO_3)_2 \rightarrow MgCO_3 \cdot CaCO_3 \qquad (8)$$

The formed magnesite (MgCO$_3$) is in a metastable state and immediately decomposes to MgO. CaCO$_3$ decomposition occurs at a higher temperature, near the calcite decomposition temperature. Independently of the mechanism of dolomite decomposition, MgO formation always occurs at the temperatures existing in a boiler ($T > 800$°C).

During heat treatment of dolomite at high CO_2 partial pressures (half-calcination), different authors [6,18] observed: (i) that the formed calcite crystals were composed of smaller crystallites; (ii) a loss of the preferential orientation of individual crystallites and a growth in size with increasing temperature and heat treatment time. These facts suggest that the half-calcination conditions (temperature, heating rate, heat treatment time, etc.) will affect the structural characteristics of dispersed calcite grains (orientation and size). In this sense, Siegel et al. [6] detected that the sulfation reactivity of half-calcined dolomite particles is affected by the preparation method.

Under the conditions existing in the boiler, MgO is inert as a desulfurant agent. At temperatures higher than 800°C, the formation of $MgSO_4$ is thermodynamically unfavorable [19]. Thus, the SO_2 equilibrium concentration at 800°C of the MgO–$MgSO_4$ system is 100 ppm (3% O_2).

From the above considerations, the following conclusions can be deduced for dolomite particles injected into a boiler: (i) $MgCO_3$ always decomposes, and in atmospheric combustors (AFBC and PC) $CaCO_3$ decomposition also occurs ($MgO \cdot CaO$), but in pressurized systems (PFBC) $CaCO_3$ calcination is inhibited ($MgO \cdot CaCO_3$); (ii) the MgO formed is inert as a desulfurant agent under the conditions existing in a boiler; (iii) in pressurized systems the sulfation of dolomite particles will occur according to Eq. (3); (iv) it is expected that the sulfation rate of half-calcined samples depends on the preparation method and, consequently, on the type of reactor in which the process takes place.

4. Results and discussion

4.1. Sulfation of dolomite particles in a thermogravimetric system

The results and discussion presented here refer to experiments in which the dolomite particles were heated at low rates (50 K min^{-1}). This is an important variable because it determines the textural development of half-calcined dolomite particles (i.e. crack formation, specific surface area, etc.) and the morphological properties of the calcite grains formed. Fuertes et al. [20] have already observed the formation of numerous cracks along the surface of uncalcined limestone particles thermally treated at 850°C in CO_2 at high heating rates (> 1000 K s^{-1}).

The dependence of fractional conversion on particle size is clearly illustrated in Fig. 5. The experiments were carried out at 866°C. The increase in particle size results in a decrease in fractional conversions and reaction rates. This behavior can be explained as a consequence of the increase of intraparticle diffusional resistance with particle diameter. In Fig. 6 the change in reaction rate with fractional conversion is represented for different particle sizes. Two different stages can be distinguished. At low degrees of conversion, high sulfation rates were measured. Once a defined conversion degree has been reached, the specific value of which decreases with particle size, the reaction rate hardly changes with conversion. This is typical behavior of calcium-based sorbents during sulfation. However, the change

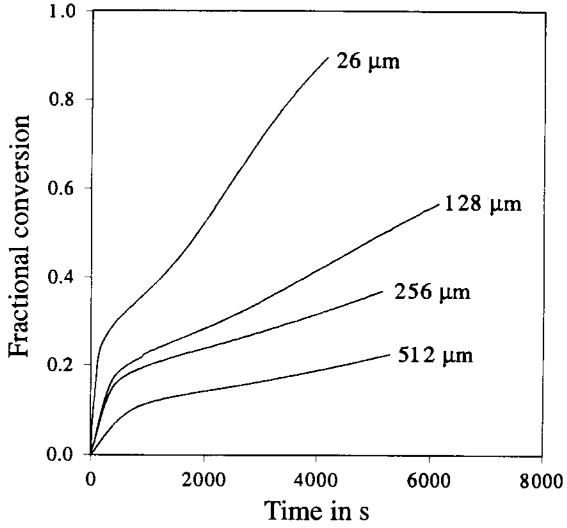

Fig. 5. Effect of dolomite particle size on the direct sulfation of dolomite particles ($T = 866°C$).

in sulfation rate shown by half-calcined dolomite particles is more abrupt than that observed for the direct sulfation of limestone particles [12]. This is clearly shown in Fig. 7, where a comparison between the reaction rates of direct sulfation of limestone and dolomite particles is presented. The half-calcined dolomite particles have high specific surface areas (5 m^2 g^{-1}) compared with those of limestone particles (0.64 m^2 g^{-1} [10]). This explains the higher initial sulfation rates of

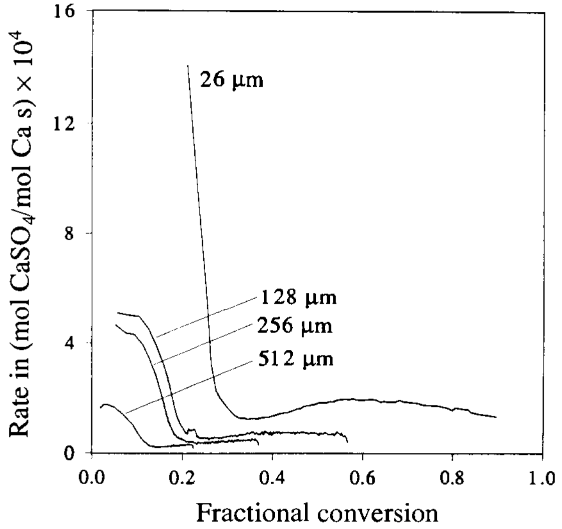

Fig. 6. Variation in sulfation reaction rate with fractional conversion for different dolomite particle sizes ($T = 866°C$).

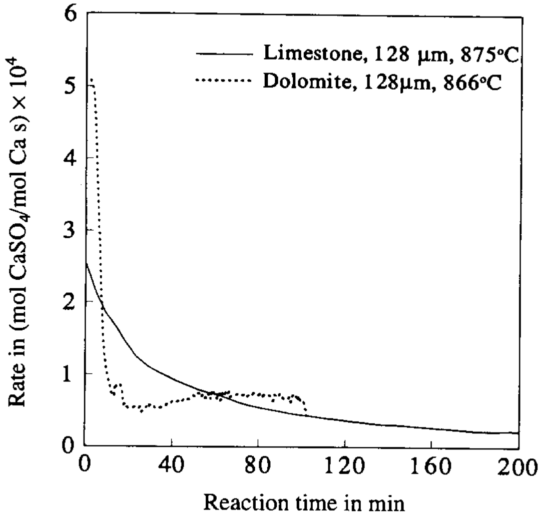

Fig. 7. Comparison between sulfation reactivity of limestone and dolomite particles.

dolomite compared with those of limestone particles. However, the half-calcined dolomite particles exhibit a very narrow porosity, with a pore radius of around 26 nm [8]. This implies that the pore plugging phenomena will take place during the first reaction stage, restricting SO_2 accessibility to the calcite crystals. Under these circumstances, an abrupt decrease in sulfation reaction rate should be expected.

In Fig. 8, the variation in fractional conversion with time at different reaction temperatures is illustrated for dolomite particles with a size of 26 μm. As observed

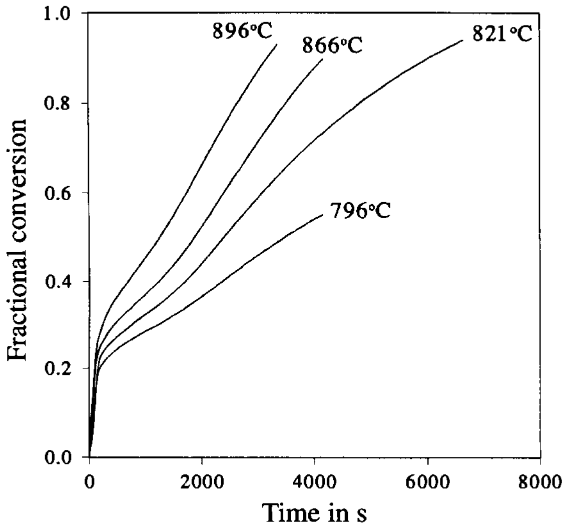

Fig. 8. Effect of reaction temperature on the direct sulfation of dolomite particles ($d_p = 26\ \mu$m).

previously (Fig. 5), two reaction stages can be distinguished. Very high reaction rates ($>2 \times 10^{-4}$ s^{-1}) are observed at all temperatures, at times below 150 s. Qualitatively, the variation in reaction rate with extent of conversion is similar to those already discussed (Fig. 6). The temperature hardly affects the reaction rate during the first reaction stage ($t < 150$ s). After this point, at fractional conversions higher than 0.25, clear differences in reactivity at different temperatures are detected.

The shape of the X–t curves (Figs. 5 and 8) is of interest because its initial slope drops off rapidly. However, after a time of around 1000 s a new increase in sulfation rate is detected (see Fig. 6). Siegel et al. [6] observed similar behavior during the sulfation of some half-calcined dolomite samples. No definitive explanation of this anomalous behavior exists, but it could be associated to the occurrence of structural changes in the calcite crystal which take place simultaneously to the sulfation reaction and, consequently, affect the reaction rate.

A comparison between the sulfation behavior of half-calcined and calcined dolomite particles was made. In Fig. 9 the variation in fractional conversion with time is represented for the sulfation of half-calcined dolomite particles and calcined dolomite particles at 821°C. During the initial reaction stage ($t < 200$ s) high sulfation rates are observed in both cases. After this point, the sulfation rates at high CO_2 partial pressure are higher than those observed in calcined dolomite particles. This fact indicates that half-calcined dolomite is a more effective desulfurant agent than calcined dolomite. Similar behavior was observed when sulfation of limestone particles, at high and low CO_2 partial pressures, was compared [9].

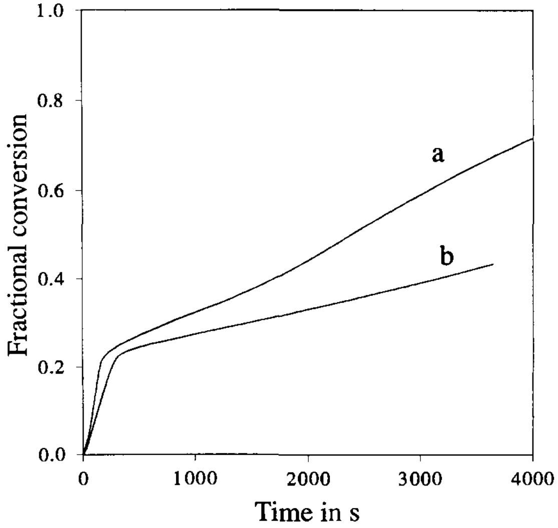

Fig. 9. Comparison of sulfation between (a) half-calcined dolomite and (b) calcined dolomite particle ($T = 821°C$; $d_p = 26$ μm).

4.2. *Sulfation of dolomite particles in a shock-microreactor*

When dolomite particles are injected into a combustor, different processes occur simultaneously. (a) Particles heated at high rates undergo thermal shock causing crack formation across the surface. (b) At a given temperature, the value of which depends on the operating conditions, the calcination and sulfation reactions occur simultaneously. In a TGA system all these processes occur separately: slow heating of the sample up to the reaction temperature (during this stage calcination of the sample takes place), followed by sulfation. Additionally, as commented before, the rearrangement of calcite crystals can be affected by the half-calcination mode. From all these facts, it is expected that both the kinetics and the sulfation capacity depend on the sulfation method. Therefore, it becomes interesting to develop a simple laboratory system to study the sulfation reaction under conditions similar to those existing in a combustor (i.e. high heating rates and simultaneous occurrence of sulfation and calcination). The SR system used in these experiments attains both conditions.

In Fig. 10 the variation in fractional conversion with time for experiments carried out in the SR system at different temperatures is displayed. As shown, the $X-t$ variations are very different from those observed in TGA experiments. In Fig. 11 a comparison between the $X-t$ data obtained in TGA and SR systems is given. Both experiments were carried out using dolomite particles with a size of 128 μm, at 860°C and in a sulfation atmosphere composed of 2600 ppm SO_2, 3.6% O_2 and CO_2. It can be seen that dolomite particles sulfated under thermal shock conditons exhibit higher sulfation rates. This clearly illustrates the importance of the measure-

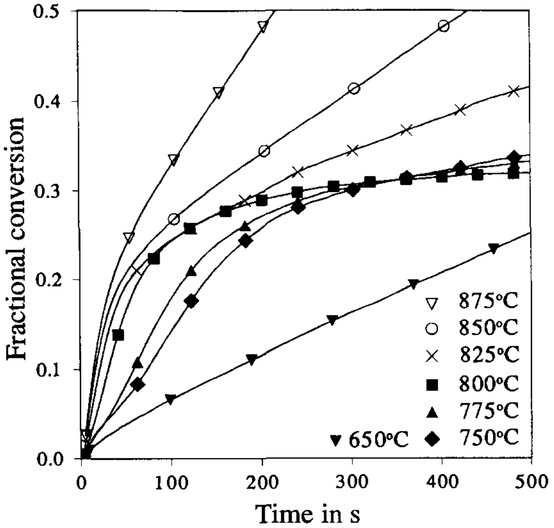

Fig. 10. Effect of reaction temperature on the variation of fractional conversion with time during SR experiments ($d_p = 128$ μm).

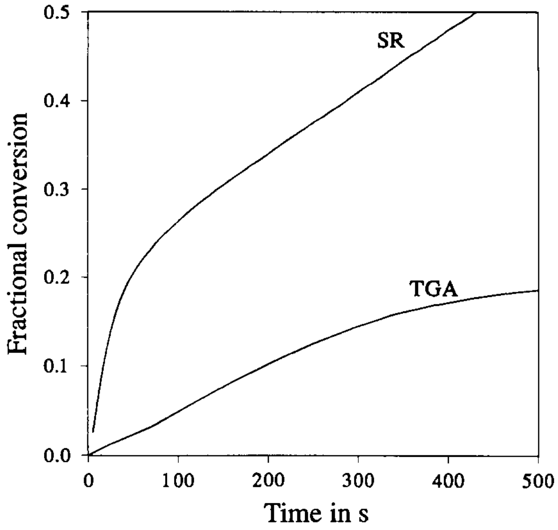

Fig. 11. Comparison of sulfation experiments of half-calcined dolomite in TGA and SR systems ($T = 860°C$; $d_p = 128$ μm).

ment method on the analysis of sulfation kinetics. These differences can be accounted for as a consequence of thermal shock. The reaction surface area increases are due to (a) formation of cracks along the surface area; (b) fragmentation of dolomite particles as a consequence of decrepitation phenomenon [21].

The SR method allows the gas flowing through the layer of dolomite particles to be considered as almost perfectly mixed due to the effect of axial molecular diffusion. Under the experimental conditions employed in the SR experiments, the Reynolds number (*Re*) is around 0.1. At this value of *Re*, molecular diffusion is the predominant dispersion mechanism. It is then possible to estimate the Peclet number according to

$$Pe = uL/D \tag{9}$$

where u is the linear velocity of gas entering the shock microreactor, L is the thickness of the particle layer and D is the molecular diffusivity of SO_2 in N_2. Under the experimental conditions used here, $Pe \approx 0.2$. For this value of Peclet's number and according to the axial dispersion model described by Levenspiel [22], the gas in the SR system can be considered as perfectly mixed. Thus, a mass balance for the SO_2 concentration of the gas before (Y_0) and after (Y) the dolomite layer, assuming perfect mixing of the gas and a first-order reaction with respect to SO_2 concentration, yields

$$\text{Sufation rate} = k_p p_{SO_2} = \frac{F_0}{n_0}(Y_0 - Y) \tag{10}$$

where k_p is the sulfation rate constant (atm SO_2 s)$^{-1}$ and p_{SO_2} is the SO_2 partial pressure (atm).

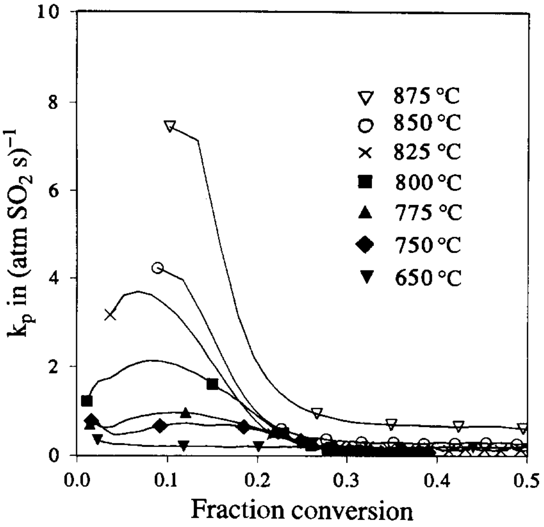

Fig. 12. Modification of rate constant with fractional conversion ($d_p = 128$ μm).

In Fig. 12 the variation in sulfation rate constant with fractional conversion is represented for experiments carried out at different reaction temperatures between 650 and 850°C. The rate constant rapidly decreases with conversion, probably due to the increase of intraparticle diffusion resistance as a consequence of pore plugging. The variation in sulfation rate constant with temperature is represented in Fig. 13 as an Arrhenius plot. An apparent activation energy value of 34 kcal mol^{-1} was obtained from the slope. This value is in agreement with those estimated by

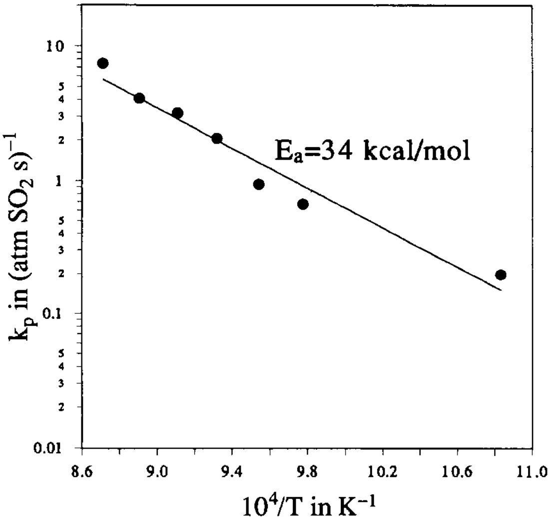

Fig. 13. Arrhenius plot for sulfation rate constant measured at $X = 0.1$ ($d_p = 128$ μm).

other authors for the direct sulfation of $CaCO_3$/limestone particles. Thus, Fuertes and co-workers [11] obtained an activation energy value of 35.4 kcal mol^{-1} for the direct sulfation of limestone particles with a diameter of 128 μm. The same authors [12] estimated a value of 27.1 kcal mol^{-1} for the reaction between reagent $CaCO_3$ particles and SO_2 at high CO_2 partial pressures. Iisa and Hupa [23] measured a value of 31.1 kcal mol^{-1} for the direct sulfation reaction of limestone particles ($d_p = 150$ μm). Hajaligol et al. [9] obtained an activation energy of 35 kcal mol^{-1}.

After the initial reaction stage, it is reasonable to suppose that the sulfation reaction is controlled by diffusion through the $CaSO_4$ product layer formed around the calcite crystals. The high values found for the activation energy of the limestone/$CaCO_3$–SO_2 reaction are not satisfactorily explained considering molecular diffusion or Knudsen diffusion through the pores. Some authors [11,23] consider that these values are consistent with a solid-state ionic diffusion mechanism. A mechanism, based on solid-state ionic diffusion, has been proposed by Fuertes et al. [11] to explain the direct sulfation of limestone/$CaCO_3$ particles. The same considerations can be argued here in relation to the direct sulfation of half-calcined dolomite particles. The measured value of the activation energy (34 kcal mol^{-1}, Fig. 13) indicates that the process is controlled by a solid-state diffusion mechanism. A mechanism, similar to that proposed by Fuertes et al. [11] to explain the direct sulfation of limestone/$CaCO_3$, can be used to understand the direct sulfation of $CaCO_3$ grains dispersed along a matrix of half-calcined dolomite particles.

It can be imagined that a non-porous $CaSO_4$ layer is formed around the calcite crystals during the sulfation of half-calcined dolomite particles. Accepting that the CO_3^{2-} ion is the mobile species in ionic diffusion through the $CaSO_4$ layer, one would expect this ion to diffuse from the $CaCO_3$–$CaSO_4$ interface to the product layer surface. At this point the following reactions can occur:

$$CO_3^{2-} \rightarrow (CO_2)_{ads} + O^{2-} \tag{11}$$

$$O^{2-} + SO_3 \rightarrow SO_4^{2-} \tag{12}$$

$$(CO_2)_{ads} \rightleftharpoons CO_{2(g)} \tag{13}$$

To maintain the neutral electrical charge in the product layer the counterdiffusion of the SO_4^{2-} species must be postulated. At the $CaCO_3$–$CaSO_4$ interface, the following reaction can then be envisaged:

$$SO_4^{2-} + CaCO_3 \rightarrow CaSO_4 + CO_3^{2-} \tag{14}$$

In order to compare the direct sulfation of dolomite and limestone particles under thermal shock conditions, some experiments were carried out with limestone particles ($d_p = 128$ μm) in the SR system. Fig. 14 compares the variation in fractional conversion with time of limestone and dolomite particles at different reaction temperatures (775, 825 and 875°C). Domolite particles exhibit higher reaction rates and consequently greater degrees of sulfation than limestone particles. This disparity can be explained by taking into account the following arguments: (a) In contrast to non-porous limestone particles, half-calcined dolomite

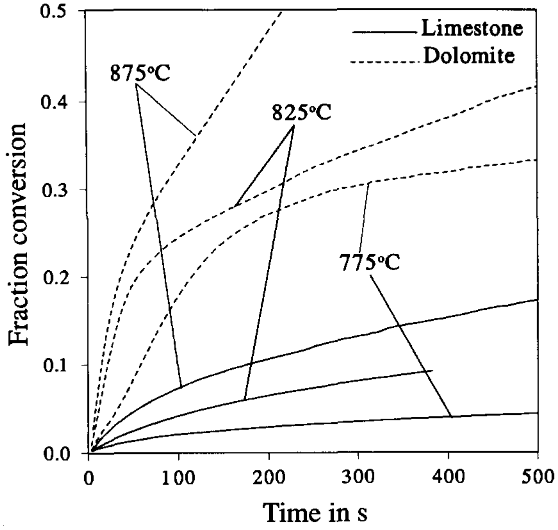

Fig. 14. Comparison between dolomite and limestone direct sulfation under thermal shock conditions ($d_p = 128$ μm).

particles have some porosity, which enhances SO_2 diffusion within the particles; comparison between the specific surface areas of limestone (0.64 m^2 g^{-1}) and half-calcined dolomite (5.0 m^2 g^{-1}) supports this fact. (b) It was observed that dolomite particles with a size above ≈100 μm break into small fragments during the heating step (decrepitation phenomenon). This circumstance facilitates the gas–solid contact due to a decrease in the intraparticle diffusion resistance.

5. Conclusions

The sulfation of dolomite particles was studied in two different experimental devices: a classical thermogravimetric analyzer (TGA) and a shock-microreactor (SR). The sulfation method has a strong influence on the reaction rate and degree of sulfation. Thus, when the sulfation reaction occurs at rapid heating rates and simultaneous calcination–sulfation (SR apparatus), the dolomite particles exhibit higher reactivities and the final degree of sulfation is also greater than the values found in TGA experiments.

Particle size was found to have a strong influence on the conversion–time profiles, indicating that the intraparticle diffusional resistance is a rate-determining step. The temperature was also found to have an important effect on the conversion–time profiles of half-calcined dolomtie particles. The conversion–time profiles for the $CaCO_3 \cdot MgO-SO_2$ reaction found in this study were markedly different from those for the $CaO \cdot MgO-SO_2$ reaction, indicating that half-calcined dolomite is a better desulfurant agent than full-calcined dolomite particles.

The value of the activation energy found from the slope of the Arrhenius plot (34 kcal mol^{-1}) indicates that the process is probably controlled by solid-state ionic diffusion through the $CaSO_4$ layer formed around the calcite crystals. In this sense, a mechanism for the sulfation reaction was proposed.

From the comparison between sulfation experiments of dolomite and limestone particles under high CO_2 partial pressures, it can be concluded that half-calcined dolomite particles exhibit higher reactivities and sulfation capacities (evaluated as mol SO_2/mol Ca) than limestone particles.

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References

[1] R.H. Borgwardt and R.H. Harvey, Environ. Sci. Technol., 4 (1972) 350.
[2] M. Hartman and R.W. Coughlin, Ind. Eng. Chem., Process Des. Dev., 13 (1974) 248.
[3] R.H. Borgwardt and K.R. Bruce, AIChE J., 32 (1986) 239.
[4] W. Jozewicz and D.A. Kirchgessner, Powder Technol., 58 (1989) 221.
[5] F. Garcia-Labiano, J. Adanez, F. Rubiera, A.B. Fuertes and J.J. Pis, Can. J. Chem. Eng., 70 (1992) 734.
[6] S. Siegel, L.H. Fuchs, B.R. Hubble and E.L. Nielsen, Environ. Sci. Technol., 12 (1978) 1411.
[7] N.H. Ulerich, R.A. Newby and D.L. Keairns, Thermochim. Acta, 36 (1980) 1.
[8] F. Rubiera, A.B. Fuertes, J.J. Pis, V. Artos and G. Marbán, Thermochim. Acta, 179 (1991) 125.
[9] M.R. Hajaligol, J.P. Longwell and A. Sarofim, Ind. Eng. Chem. Res., 27 (1988) 2203.
[10] A.B. Fuertes, G. Velasco, E. Fuente, J.B. Parra and T. Alvarez, Fuel Process Technol., 36 (1993) 65.
[11] A.B. Fuertes, G. Velasco, E. Fuente and T. Alverez, Fuel Process Technol., 38 (1994) 181.
[12] A.B. Fuertes, G. Velasco, M.J. Fernandez and T. Alvarez, Thermochim. Acta, 242 (1994) 161.
[13] K. Iisa and M. Hupa, 23rd Symp (Int.) on Combustion, The Combustion Institute, Orleans, 22-27 July 1990, p. 943.
[14] E. Erdös, Collect. Czech. Chem. Commun., 27 (1962) 2152.
[15] E.H. Baker, J. Chem. Soc., (1962) 464.
[16] R.M. McIntosh, J.H. Sharp and F.W. Wilburn, Thermochim. Acta, 165 (1990) 281.
[17] B.G. Hurd, Anal. Chem., 35 (1963) 1468.
[18] R.A.W. Haul and H.G.F. Wilsdorf, Nature (London), 167 (1951) 945.
[19] E.W. Dewing and F.D. Richardson, Trans. Faraday Soc., 55 (1959) 611.
[20] A.F. Fuertes, G. Marbán and F. Rubiera, Chem. Eng. Res. Des., 71A (1993) 421.
[21] R.A. McCauley and L.A. Johnson, Thermochim. Acta, 185 (1991) 271.
[22] O. Levenspiel, Ingenieria de las racciones químicas, 2nd edn., Reverte, Barcelona, 1988, p. 304.
[23] K. Iisa and M. Hupa, FBC Technology and the Environmental Change, Adam Hilger, London, 1991, p. 191.