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The effect of metallic salt additives on direct sulfation of calcium carbonate and on decomposition of sulfated samples

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Abstract

The effect of different types of metallic salt additives (Na_2CO_3, Li_2CO_3, K_2CO_3, Na_2SO_4, NaF, NaCl, $ZnSO_4$, $Ca(NO_3)_2$, Cs_2CO_3 and $Al_2(SO_4)_3$) on direct sulfation of calcium carbonate is investigated. The experiments were carried out in a thermogravimetric analyzer under isothermal conditions at temperatures between 700 and 875°C. An ultrapure calcium carbonate sample with a mean size of 17 μm and a specific surface area of 0.43 $m^2 g^{-1}$ was used. From the sulfation tests some additives (Na_2CO_3, Li_2CO_3, K_2CO_3, Na_2SO_4, NaF, NaCl) enhanced the sulfation capacity and sulfation rate with respect to the undoped sample. All these additives correspond to alkaline compounds. The effect of additives on the decomposition of $CaSO_4$ in sulfated samples was also investigated. In this case nonisothermal experiments with a heating rate of 4 K min^{-1} were performed in a CO_2 atmosphere. The results indicate that presence of some additives has a catalytic effect on sulfate decomposition.

Keywords: Additives; Calcium carbonate; Metallic salts; Sulfation; TGA

1. Introduction

Combined cycle is a promising technology for power generation which is expected to contribute a considerable share of the electricity supply by the year 2000. Presently, different aspects related to hot gas cleaning in combined cycles are under investigation, mainly sulfur and alkali removal at high temperatures (> 500°C). Thus, the control of sulfur emissions (SO_2 in combustion and H_2S in gasification systems) constitutes an

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important task in the development of this technology. In the case of pressurized fluidized combustion systems (PFBC) which constitute a relevant combined cycle category, the sulfur emitted (as SO_2) is retained by means of calcium-based sorbents (i.e., limestone or dolomite). In this type of reactor, the combustion occurs in a bubbling or circulating fluidized bed operating at temperatures of 800–900°C and pressures up to 1.2 MPa. Under these conditions, the CO_2 partial pressure is around 0.1 MPa and, in consequence, the $CaCO_3$ decomposition is not favored thermodynamically. Then, the sulfation reaction will take place according to the following scheme

$$CaCO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$$

Analysis of the kinetics of the $CaCO_3$–SO_2 reaction has been performed by Snow et al. [1], Hajaligol et al. [2], Iisa and coworkers [3,4], Illerup et al. [5], Tullin et al. [6], and Fuertes and coworkers [7–10]. From these studies it has been concluded that: (a) the direct sulfation of $CaCO_3$ particles enables higher degrees of sulfation than those observed from sulfation of CaO particles; (b) for short reaction times the process takes place under chemical control (measured activation energies around 17–25 kcal mol^{-1}). For longer reaction times, diffusion through the product layer becomes the controlling step. The measured values for the activation energy at this stage (around 30–35 kcal mol^{-1}) suggest that diffusion probably takes place by means of a solid-state ionic diffusion mechanism rather than a molecular or Knudsen diffusion model. Fuertes et al. [8] proposed a mechanism for this reaction in which the CO_3^{2-} is assumed to be the mobile species in ionic diffusion through the $CaSO_4$ layer.

Ionic diffusion is a complex phenomenon that has been studied extensively [11,12] in the context of metallic oxidation. No mechanistic studies of diffusion through $CaSO_4$ have been reported. It is, however, well-established that the rate of diffusion in a solid is associated with lattice defects (impurities or defects in the crystal structure), so it should be expected that the presence of impurities or crystal defects would affect the sulfation reaction of Ca-based sorbents. Thus, it has been noticed that limestones with a similar $CaCO_3$ content exhibit very different behavior during sulfation. This can be attributed to the role that impurities or crystal characteristics plays during the stages of calcination and sulfation [13]. In this context the literature offers numerous examples of the enhancement of SO_2 sorption on CaO by the addition of different types of additive, mainly alkaline compounds [13–18]. The presence of impurities affects the textural characteristics (porosity and surface area) of the CaO formed during calcination of limestone particles owing to the sintering of nascent CaO grains, accelerated by the presence of foreign ions [13]. In consequence, the modification of sulfation of CaO particles by the addition of doping additives is the result of two different contributions: (a) modification of textural characteristics during the calcination stage and (b) modification of the intrinsic rate of sulfation.

No significant studies have been reported about the effect of inorganic additives on the direct sulfation of calcium carbonate. In this case, because the process takes place under conditions where calcination is inhibited, the effect of doping ions on sulfation can be more clearly analyzed. The main objective of this paper is to investigate the influence of different additives (inorganic salts) on the direct sulfation of doped pure calcium carbonate particles. In addition, the effect of the impurities on the decomposition rate and the stability of sulfated samples will be examined.

2. Experimental

The experiments were performed with ultrapure $CaCO_3$ (Suprapur calcium carbonate Merck, no. 2059). The total metallic and nonmetallic impurities are certified to be less than 300 ppm. The particle size distribution was determined by using a Coulter Multisizer II, ranging between 5 and 30 µm, with a mean particle diameter of 17 µm (std. dev., 5.1 µm). The BET surface area, measured in nitrogen (−196°C), was 0.43 $m^2\,g^{-1}$.

In order to study the effect of impurities on the sulfation reaction, the calcium carbonate particles were doped with different metallic salts: Li_2CO_3, Na_2CO_3, K_2CO_3, Cs_2CO_3, $Al_2(SO_4)_3$, $Zn(SO_4)$, $Ca(NO_3)_2$, NaCl, NaF, and Na_2SO_4. All compounds were purchased from Merck and contained very low impurity levels (<1%). In the doped calcium carbonate samples the atomic (Ca : metallic element (Me)) ratio was fixed at a value of 15. The additive was deposited over $CaCO_3$ particles by evaporating an aqueous solution containing the required amount of salt (Ca : Me ratio 15). In order to obtain uniform distribution of the salt on the $CaCO_3$ particle surface, the slurry was continuously stirred during the drying stage. Finally, the dry sample was ground in order to destroy the agglomerates and restore the original particle size.

A thermogravimetric analyzer (Setaram Tag 24) was used in these experiments. The experimental procedure consisted in heating a sample at 40°C min^{-1}, in a CO_2 atmosphere, up to the desired temperature. When the isothermal condition was reached, a gas stream with a composition of 2000 ppm SO_2 and 2.7% O_2 was added. The gas composition was balanced with CO_2 (direct sulfation). In all experiments the sample weight was below 5 mg and the gas flow rate 100 $cm^3\,min^{-1}$. Under these conditions, the reaction rate was found to be independent of external influences.

The decomposition of sulfated samples was studied under nonisothermal conditions (heating rate 4 K min^{-1}) in an atmosphere of CO_2 (gas flow rate 75 $cm^3\,min^{-1}$).

3. Results and discussion

3.1. Effect of additives on sulfation loading

The influence of additives on sulfur capture is summarized in Table 1. A ranking of the sulfation ability of doped sorbents can be established, from the conversion data after 30 min.

$$Na_2CO_3 > Li_2CO_3 > K_2CO_3 > Na_2SO_4 \approx NaF > NaCl > \text{no additives} >$$

$$ZnSO_4 \approx Ca(NO_3)_2 > Cs_2CO_3 \approx Al_2(SO_4)_3$$

The sulfation rate of different samples measured at $X = 0.2$ exhibits a similar trend. From these data it is clear that additives which contain alkali metals (except Cs)

Table 1
Sulfur capture and reactivity of doped calcium carbonate samples ($T = 850°C$; SO_2, 2000 ppm; O_2: 2.7%; rest CO_2)

Additive	Fractional conversion		Reactivity at $X = 0.2 \times 10^4/s^{-1}$	$(dX/dt)_{doped}/(dX/dt)_{CaCO_3}$ (at $X = 0.2$)
	$t = 30$ min	$t = 60$ min		
–	0.43	0.58	3.32	1
Li_2CO_3	0.70	0.99	5.48	1.65
Na_2CO_3	0.78	1	5.52	1.63
K_2CO_3	0.68	0.87	4.96	1.49
Cs_2CO_3	0.25	0.30	0.96	0.29
NaCl	0.60	0.89	3.91	1.18
NaF	0.64	0.94	4.67	1.40
Na_2SO_4	0.65	0.92	4.36	1.31
$ZnSO_4$	0.40	0.53	2.83	0.85
$Al_2(SO_4)_3$	0.27	0.40	1.05	0.32
$Ca(NO_3)_2$	0.40	0.59	2.24	0.67

enhance the capture of sulfur by calcium carbonate. On the other hand, nonalkali metal additives show a negative effect on SO_2 capture. A question arises as to whether the increase in sulfur removal is a result of enhancement of the process or may be attributed to formation of alkali sulfate from the additive compound. From a simple balance and considering that all the additive is sulfated, it was verified that this contribution to the measured conversions is approximately 0.03. This indicates that the observed enhancement or reduction of SO_2 removal is greater than that attributed to SO_2 removal by the additive alone.

The variation of sulfation degree with time is represented in Fig. 1 for all doped samples. From this figure strong differences are detected for the different doped sorbents. In principle two groups can be distinguished: (i) alkaline compounds (except Cs_2CO_3) which either enhance or do not significantly modify in the rate of sulfur capture relative to pure calcium carbonate and (ii) additives which have a negative effect on sulfur capture. These are salts of heavy metallic elements (Cs) or di/trivalent elements (Zn, Al).

The promoting effect of the additives can be better understood by taking into account the role that impurities play in the sulfation reaction. However, some controversy exists about the effective promoting mechanism. Thus, Slaughter et al. [17] explained the positive effect that the presence of sodium compounds exert on the sulfation of CaO by considering that the sodium reacts with the CaO matrix to induce particle fragmentation and the formation of large cracks, thereby increasing the number of calcium oxide sites that are readily available. On the other hand, the possible promoting mechanism proposed by Muzio et al. [15] is based upon the volatilization of the alkali, formation of sulfates, transport to the sorbent surface, and creation of a melt layer due to the eutectics formed. According to these authors, the transport of SO_2 and O_2 into and through the melt layer is enhanced, promoting the rate of sulfation. Taking

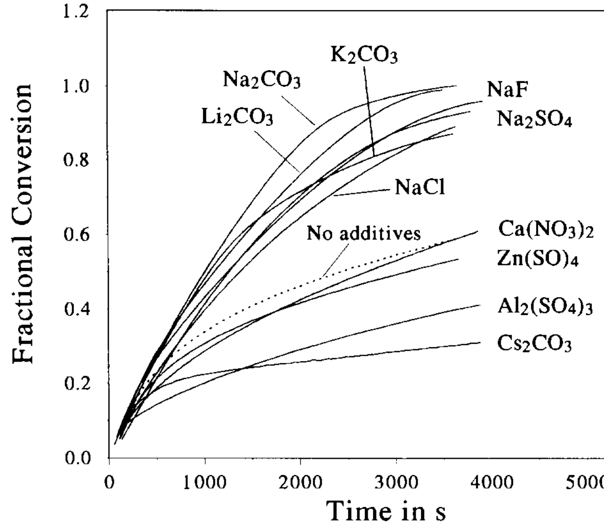

Fig. 1. Influence of additives on the variation of fractional sulfation with time. Reaction temperature: 850°C.

into account that CaO formation does not take place when the sulfation occurs at high CO_2 partial pressures, as used in this study, the mechanism indicated by Muzio et al. [15] seems more appropriate under our conditions than the Slaughter model.

However, some uncertainties remain in regard to the application of this mechanism to our experiments. Thus, Muzio's mechanism is not consistent with the kinetic data reported by different authors [2,8,19]. These studies suggest that solid-state diffusion through the product layer is the controlling reaction step for direct sulfation. This result is difficult to reconcile with the model proposed by Muzio et al. [15] to explain the promoting effects. Another possible interpretation of the promoting effect of impurities was given by Borgwardt et al. [13]. These authors consider that the effect is a consequence of enhancement of solid-state diffusion by the foreign ions incorporated into the growing $CaSO_4$ product; this causes the formation of lattice defects and promotes the movement of ions. This hypothesis is more consistent with the proposed mechanism for direct sulfation of calcium carbonate particles. However, the observed decrease in sulfur loading and reaction rate for samples doped with some types of impurity (e.g. Zn, Al, Cs), relative to pure calcium carbonate, is not explained by this hypothesis.

3.2. *Effect of the addition of Na_2CO_3 on sulfation rate*

From the data shown in Table 1 and Fig. 1 sodium carbonate furnishes the maximum enhancement of sulfur capture. A more comprehensive study of the effect of Na_2CO_3 on direct sulfation of calcium carbonate particles is presented in this section. The variations of fractional conversion with time for $CaCO_3$ and Na_2CO_3-doped $CaCO_3$, at different reaction temperatures between 700°C and 875°C are represented in Fig. 2. From the indicated data it is clear that the addition of Na_2CO_3 enhances SO_2

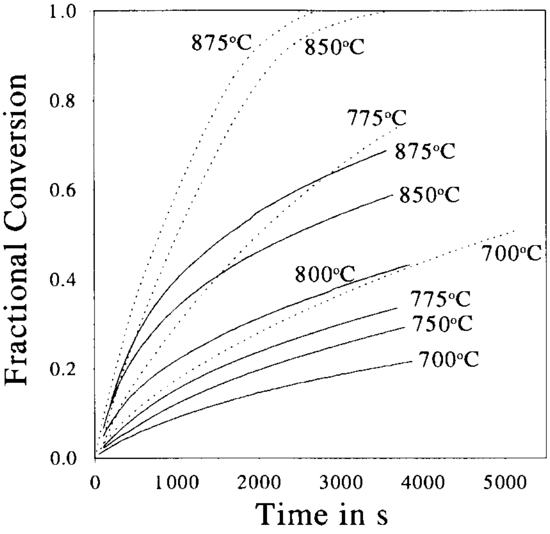

Fig. 2. Effect of temperature on conversion–time curves for samples of $CaCO_3$ and $CaCO_3$ doped with Na_2CO_3. Solid line, pure $CaCO_3$; dashed line, Na_2CO_3-doped $CaCO_3$.

capture at all reaction temperatures. The samples doped with Na_2CO_3 exhibit higher sulfation rates than pure calcium carbonate. This is more clearly illustrated in Fig. 3 where the variation of relative reaction rates with conversion is represented at different reaction temperatures. It is observed that at all temperatures the sulfation rate ratio

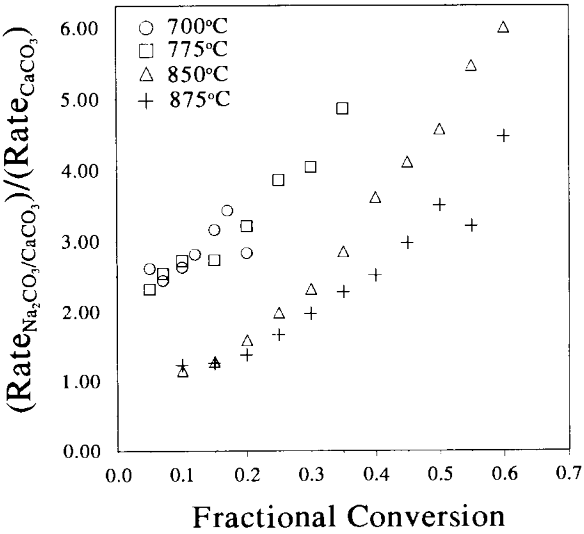

Fig. 3. Comparison between sulfation rates of pure calcium carbonate and Na_2CO_3-doped $CaCO_3$.

increases with degree of sulfation. This suggests that the enhancement of sulfation by doping ions is more pronounced once the product layer has been formed and consequently the promoting effect of impurities becomes greater once the sulfation of pure $CaCO_3$ becomes diffusion-controlled. This result can be interpreted as enhancement of solid-state diffusion by foreign ions, according to the mechanism suggested by Borgwardt et al. [13]. Evidently, this effect will be more marked as the reaction progresses and the resistance of the product layer increases, as can be seen in Fig. 3.

The variation of reaction rate with temperature for both samples (pure calcium carbonate and Na_2CO_3-doped $CaCO_3$) is represented in Fig. 4 as an Arrhenius plot at a conversion degree of 0.2. At this conversion degree the product layer is assumed to be well developed and consequently the diffusion process is supposed to play an important role in overall reaction control. As indicated before, Fig. 4 shows clearly that the reaction rates of doped samples are greater than those of pure calcium carbonate at all temperatures. Additionally, the activation energy value measured for the doped sample (23.0 kcal mol^{-1}) is lower than that found for the nondoped samples (33.5 kcal mol^{-1}). The measured activation energy for the sulfation of pure calcium carbonate (33.5 kcal mol^{-1}) is very close to activation energies reported by different authors for direct sulfation of Ca-based sorbents: 34.9 kcal mol^{-1} (pure calcite) [2], 31.8 kcal mol^{-1} (limestone) [19], and 35.4 kcal mol^{-1} (limestone) [8]. These high values of activation energy constitute an argument in favor of the proposal that diffusion through the product layer takes place according to a solid-state diffusion mechanism rather than molecular diffusion (activation energies around 2.9 kcal mol^{-1}) or a Knudsen diffusion model (activation energy around 1 kcal mol^{-1}). On the other hand, different authors [1,2,7,19] have observed that the activation energy values measured for direct sulfation under chemical control (at the onset of sulfation) are in the range 17–24 kcal mol^{-1}.

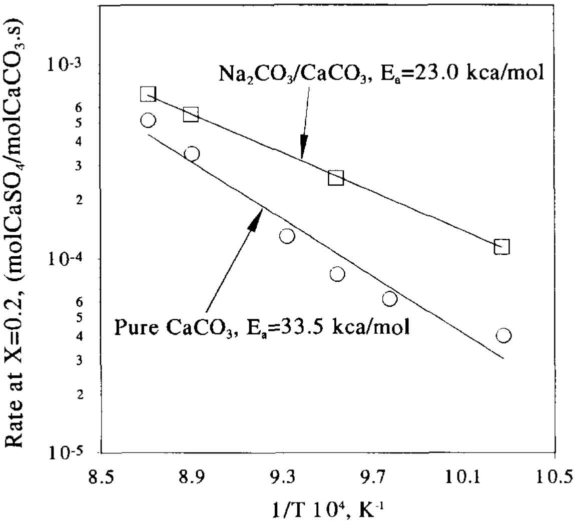

Fig. 4. Change of sulfation rate with temperature at $X = 0.2$.

The activation energy found here for sulfation of Na_2CO_3-doped calcium carbonate (23 kcal mol^{-1}) is in that range. This suggests that the overall reaction changes from diffusional control to chemical reaction control in the presence of Na_2CO_3 because of the effect of foreign ions in accelerating the solid-state diffusion.

3.3. *Effect of additives on the thermal decomposition of sulfated samples*

The thermal decomposition of inorganic substances can be influenced by the presence of some kinds of additive. Thus, it is known that some oxides of transition elements have catalytic activity during the thermal decomposition of potassium perchlorate [20]. Mu and Perlmutter [21] observed that the addition of NaCl to zinc sulfate (molar ratio 1:1) reduced the temperature of decomposition of the sulfate.

The thermal stability of calcium sulfate in partially sulfated sorbents constitutes an important aspect to be considered in relation to injection of Ca-based sorbents in the combustion furnace. Thus, in order to optimize sulfur capture a compromise between sorbent reactivity and sulfate stability is required. Encouraged by these considerations, this section analyzes the effect of doping substances on the thermal stability and decomposition rate of the calcium sulfate formed.

The effect of impurities on the decomposition of the $CaSO_4$ formed is illustrated in Fig. 5. The presence of impurities hardly affects the onset of decomposition. This occurs at a temperature around 1050°C, except in the case of Cs_2CO_3 where the onset of sulfate decomposition takes place at lower temperatures (around 1000°C). On the other hand, the presence of additives clearly modifies the decomposition rate of sulfated samples. Thus, it was observed that some impurities enhance the decomposition rate (Fig. 5a). Except for K_2CO_3, the impurities with an accelerating effect on decomposition are substances which showed a negative effect during the sulfation stage. The rest of the additives show a slight negative effect on the decomposition rate of sulfated samples (Fig. 5b). Only the sample doped with NaCl does not exhibit any difference relative to sulfated pure calcium carbonate.

The decomposition rate of partially sulfated calcium carbonate particles can be modeled according to a shrinking unreacted core model. In this case and considering that $CaSO_4$ forms a spherical layer around the $CaCO_3$/CaO unreacted core, the deduced kinetic expression for the decomposition rate can be written as

$$\frac{\mathrm{d}X}{\mathrm{d}t} = A(1 - XX_s)^n \exp\left(-\frac{E}{RT}\right) \tag{1}$$

X_s being the fractional conversion reached during the sulfation stage, X the fraction of sulfate decomposed, A the preexponential factor, and E the activation energy; n is the exponential factor, sometimes called the “reaction order”. Some authors consider this factor to have purely empirical significance [22]; in the case of reactions occurring according to the unreacted shrinking core mechanism, however, it reflects the geometric shape of the reacting particles (2/3, 1/2 and 0 for spheres, long cylinders and infinite slabs, respectively) [23]. From observations of calcium carbonate particles by scanning electronic microscopy, a spherical geometry was selected for modeling the particle shape and consequently a value of $n = 2/3$ was taken.

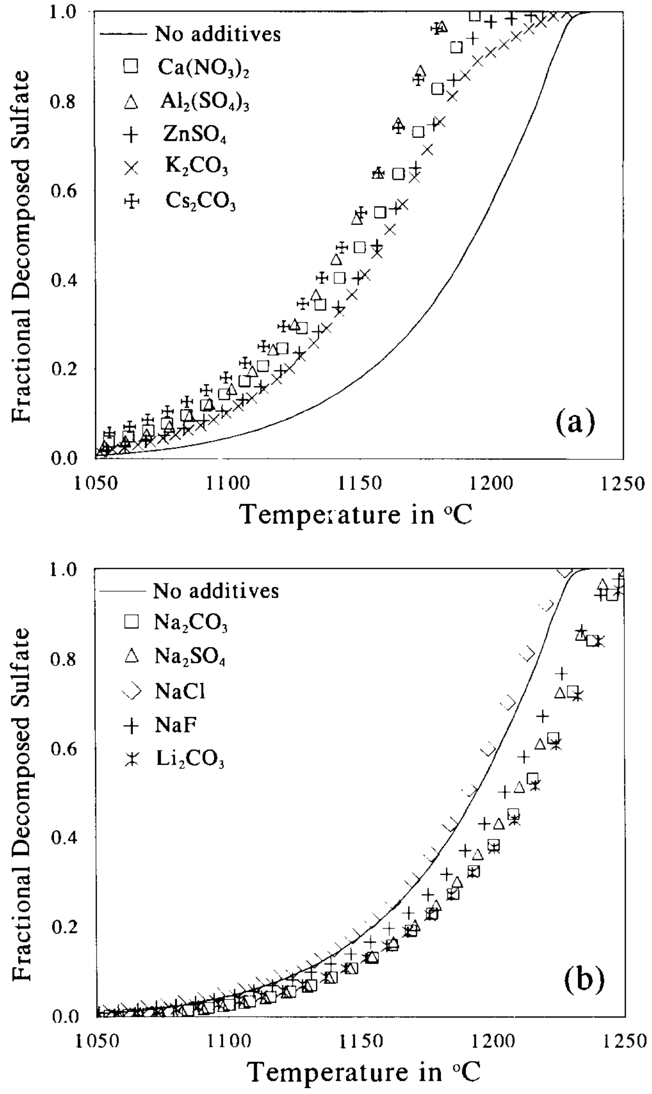

Fig. 5. Effect of additives on decomposition of sulfated samples: (a) enhancing additives, (b) inhibiting additives.

The kinetic parameters for the decomposition process (A and E) were obtained by fitting the experimental data to Eq. (1) rearranged to linear form. As an example, Fig. 6 shows the determination of the kinetic parameters from the experimental data of decomposition of sulfated samples of pure calcium carbonate. The activation energy E and the preexponential factor A, determined from the slope and intercept, were found to be 103.8 kcal mol^{-1} and 3.08×10^{12} s^{-1}, respectively.

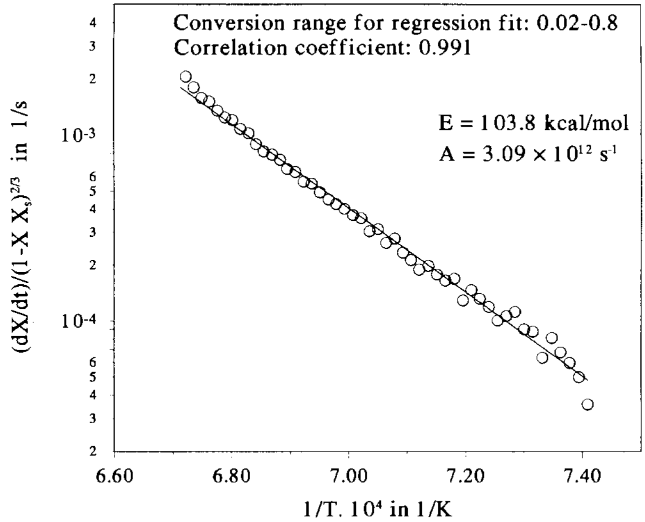

Fig. 6. Kinetic correlation for the decomposition of sulfated pure calcium carbonate particles.

By considering that the partially sulfated particles have a spherical shape and decompose according to a shrinking unreacted core model, the following relationship for the preexponential factor A can be deduced

$$A = \frac{6k_0}{d_p \rho X_s} \tag{2}$$

k_0 being the frequency factor of the decomposition rate constant k ($= k_0 \exp(-E/RT)$), d_p the particle diameter (17 μm) and ρ the density of calcium sulfate (1.91×10^4 mol m^{-3}). From the values obtained for the activation energy and preexponential factor in Fig. 6, and using Eq. (2) to obtain the parameter k_0, the following expression is obtained for the decomposition rate constant of calcium sulfate in pure sulfated $CaCO_3$ samples

$$k(\text{mol m}^{-2}\text{ s}) = 1.50 \times 10^{11} \exp\left(-\frac{103800}{1.987\,T}\right) \tag{3}$$

A comparison between the values of the reaction rate constant found here (Eq. (3)) and those achieved by Fuertes and Fernandez [24] from isothermal experiments on the decomposition of pure calcium sulfate particles in nitrogen, is represented in Fig. 7. There is acceptable agreement between both sets of values.

A summary of the corresponding kinetic parameters (E, A, k_0) for sulfate decomposition of all doped samples is given in Table 2. From these data it can be seen that the samples doped with additives with an enhancing effect during decomposition of sulfated samples (Fig. 5a) present the lowest values of activation energy ($Ca(NO_3)_2$, 83.9 kcal mol^{-1}; $Al_2(SO_4)_3$, 91.1 kcal mol^{-1}; $ZnSO_4$, 88.6 kcal mol^{-1}; Cs_2CO_3,

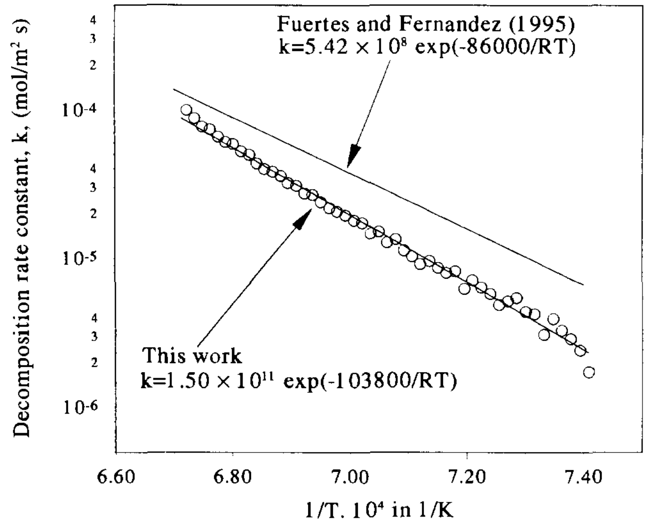

Fig. 7. Comparison of decomposition rate constants of pure calcium sulfate and a sulfated sample of calcium carbonate.

Table 2
Kinetic parameters of calcium sulfate decomposition of doped samples

Additive	Conversion range for regression fit	Correlation coefficient	Activation energy (E)/kcal mol^{-1}	Preexponential factor/(A)/s^{-1}	k_0/ (mol m^{-2} s)
–	0.02–0.80	0.991	103.8	3.08×10^{12}	1.50×10^{11}
Li_2CO_3	0.02–0.80	0.987	98.1	2.73×10^{11}	1.48×10^{10}
Na_2CO_3	0.01–0.75	0.993	101.7	1.55×10^{12}	7.97×10^{10}
K_2CO_3	0.02–0.68	0.987	93.5	1.61×10^{11}	4.15×10^{9}
Cs_2CO_3	0.02–0.90	0.992	79.2	1.19×10^{9}	1.95×10^{7}
NaCl	0.01–0.88	0.989	103.7	3.35×10^{12}	1.61×10^{11}
NaF	0.02–0.67	0.992	97.7	2.80×10^{11}	1.45×10^{10}
Na_2SO_4	0.01–0.77	0.994	107.8	8.80×10^{12}	4.43×10^{11}
$ZnSO_4$	0.02–0.85	0.995	88.6	2.89×10^{10}	8.29×10^{8}
$Al_2(SO_4)_3$	0.03–0.75	0.995	91.1	9.50×10^{10}	2.06×10^{9}
$Ca(NO_3)_2$	0.02–0.77	0.995	83.9	5.84×10^{9}	1.36×10^{8}

79.2 kcal mol^{-1}; K_2CO_3, 93.5 kcal mol^{-1}). This result suggests that the presence of these compounds exerts some type of catalytic effect on the decomposition of calcium sulfate. On the other hand, the samples with additives with an inhibiting effect upon sulfate decomposition present activation energies around 100 kcal mol^{-1}, which are very similar to that measured for the sulfated calcium carbonate sample (103.8 kcal mol^{-1}).

4. Conclusions

From the variation of sulfate loading during direct sulfation of doped calcium carbonate samples at 850°C, the following ranking can be established to describe the effect of different metallic salts upon direct sulfation

$$Na_2CO_3 > Li_2CO_3 > K_2CO_3 > Na_2SO_4 \approx NaF > NaCl > \text{no additives} >$$

$$ZnSO_4 \approx Ca(NO_3)_2 > Cs_2CO_3 \approx Al_2(SO_4)_3$$

The hypothesis that the additives cause a change in solid state diffusion during sulfation provides a consistent basis for interpretation of the results obtained.

From the comparison between direct $CaCO_3$ sulfation and Na_2CO_3-doped $CaCO_3$ sulfation, it is deduced that doped samples exhibit higher sulfation rates than pure calcium carbonate during sulfation at all investigated temperatures (between 700 and 875°C). Comparison of the activation energy for Na_2CO_3-doped $CaCO_3$ (23 kcal mol^{-1}) and that of the undoped sample (33.5 kcal mol^{-1}) suggests that the presence of a doping agent has a catalytic effect on the sulfation reaction. The fact that the measured value of the activation energy for Na_2CO_3-doped $CaCO_3$ is close to those corresponding to chemical control indicates that additives accelerate the solid-state diffusion and, in consequence, the overall reaction changes from diffusional control to chemical control.

The temperature of onset of decomposition of calcium sulfate in doped samples is not affected by the presence of additives. It has, however, been observed that the doping agents have a clear effect upon the decomposition rate. Some additives accelerate the decomposition of sulfated samples. These are the additives which exhibited a negative effect during the sulfation reaction. The measured activation energies for the sulfate decomposition are in the range 80–107 kcal mol^{-1}. The lowest values correspond to substances which exhibit an accelerating effect during sulfate decomposition, which suggests that the additives exert some type of catalytic effect upon sulfate decomposition.

Acknowledgement

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