FORMATION BEHAVIOR OF CaSO₃ DURING HIGH-TEMPERATURE DESULFURIZATION WITH Ca-BASED SORBENTS

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The effect of temperature and O_2 concentration on the product distribution of the $CaO-SO_2$ reaction was thermogravimetrically studied. The accompanied changes in pore characteristics (specific surface area and pore volume) with reaction temperature, time and O_2 concentration were also investigated. Among the sulfation products, $CaSO_3$ was found to be thermally stable at temperatures below about 973 and 1015 K with and without O_2, respectively.

Within $CaSO_3$ stability limits, O_2 presence increased the initial sulfation rate, but virtually suppressed SO_2-sorption capacity. On the other hand, at temperatures beyond $CaSO_3$ stability limits, O_2 presence improved the initial sulfation rate as well as SO_2-sorption capacity, and the reaction order with respect to SO_2 was determined to be around unity independent of O_2 presence.

Regardless of O_2 presence, the reaction order with respect to SO_2 was found to increase from 0.5 to 1.1 with temperature increase from 823 to 1123 K. No influence of O_2 concentration on the initial reaction rates and sorption capacities were observed above 2 vol% O_2 in the tested temperature range (823-1123 K). The temperature dependency of the $CaO-SO_2$ reaction system was correlated with an activation energy, E, ranging between 31 and 51 kJ·mol⁻¹.

Introduction

Recently, hydrated lime $(Ca(OH)_2)$ has been investigated widely as a potential material for sulfur dioxide (SO_2) retention owing to its high reactivity. The high porosity of calcium oxide (CaO), derived from $Ca(OH)_2$, has been documented through numerous researches (Al-Shawabkeh *et al.*, 1994a,b; Al-Shawabkeh *et al.*, 1995; Bortz and Flament, 1984; Cole *et al.*, 1987; Newton, 1987). These investigations, however, were carried out under oxidizing conditions (at around 20 vol% excess air) especially for *in-situ* dry sorbent injection technologies. Under these conditions, SO_2 capture was simply represented via the following overall reaction:

$$CaO + SO_2 + \frac{1}{2}O_2 \Rightarrow CaSO_4 \qquad (1)$$
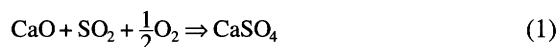
In contrast to this, desulfurization under reducing conditions (lean O_2 concentration) has been paid scant attention, despite its increasing importance. One emerging application, for instance, could be coal Fluidized-Bed Combustion (FBC) with *air staging* in order to reduce NO_x emissions. In the low O_2 concentration regime (less than 10^{-12} atm), located below the secondary air inlet, the SO_2-sorption capacity is most likely to be different from that prevailing in the oxidizing regime, above the secondary air inlet. Ljungström (1985) and Cooper and Ljungström

(1987) measured the *in-situ* O_2 partial pressure along the riser of a Circulating Fluidized-Bed Combustor (CFBC). They found the O_2 pressure to be less than 10^{-10} bar for about 80-90% of the sorbent residence time. This is why examining the O_2 concentration effect on the $CaO-SO_2$ sulfation reaction and the accompanying changes in the pore-characteristics is said to be of great importance.

Further, during desulfurization at temperatures below about 1023 K, the reaction of CaO with SO_2 becomes complicated, and overall reaction (1), therefore, fails to account for a comprehensive interpretation of the $CaO-SO_2$ reaction kinetics. This is, most likely, due to the formation of different products, namely $CaSO_3$, CaS, and/or $CaSO_4$, of different mole fractions that vay not only with temperature, but also with the presence of O_2.

Literature on the effect of O_2 on $CaO-SO_2$ sulfation product distribution and reaction kinetics is scarce. In an O_2-free atmosphere, Chan *et al.* (1970) investigated the CaO reaction with 5 vol% SO_2. At temperatures slightly higher than 473 K, $CaSO_3$ was formed. At temperatures between 773 K and 973 K, $CaSO_3$ started disproportioning into $CaSO_4$ and CaS. Marsh and Ulrichson (1985) studied the CaO reaction with 0.25-8.0 vol% SO_2 with and without 20 vol% O_2. The reaction order with respect to SO_2 was estimated to be zero and unity at temperatures below 723 K and above 1013 K, respectively.

In the current experimental study, investigations were focused on measuring the product distribution of the CaO-

Table 1 Chemical and physical properties of calcium hydroxide

ρ (kg·m^{-3})	2.20×10^3
d_p (μm)	20
Sa (m^2·kg^{-1})*	33.1×10^3
Va (m^3·kg^{-1})*	15.5×10^{-5}
r_p (nm)*	9.3

Chemical composition (wt%)

HCl	0.01%
Cl	0.01%
SO$_4$	0.05%
Pb	0.001%
Fe	0.01%
As	0.00005%
Assay	97.0%

*BET adsorption techniques of Ca (OH)$_2$ calcined at 1123 K

Fig. 1 Typical weight-time curves of Ca (OH)$_2$ calcination, CaO sulfation, and CaSO$_3$ decomposition reactions

SO$_2$ reaction. The effect of product distribution change, with temperature and O$_2$ concentration, on the initial reaction kinetics was also probed. The associated changes in the pore-structural characteristics with sulfation progress are provided. The test temperatures ranged from 823 to 1123 K. The concentrations of the gaseous reactants were varied from 0.11 to 0.31 vol% for SO$_2$, and from 0 to 10 vol% for O$_2$. All calcination and sulfation runs were carried out with a thermogravimetric analyzer.

1 Experimental section

1.1 Experimental apparatus

A thermogravimetric analyzer (TGA 50, Shimadzu Corporation, Kyoto, Japan) equipped with a computerized monitor was employed for kinetic measurements. A sulfation gas mixture was simulated as 0.11-0.31 vol% SO$_2$, 0-10 vol% O$_2$, and balance N$_2$ by adjusting each individual gas using a precalibrated rotameter. Detailed description of the experimental setup can be found in our previous works (Al-Shawabkeh *et al.*, 1994a, b)

1.2 Test sorbent

A commercial reagent grade of hydrated lime (Ca (OH)$_2$, Katayama Chemicals, Osaka, Japan, Code No. 05-0740) was used in this study. The mass mean diameter of Ca(OH)$_2$ was measured as 20 μm. The pore physical properties (specific surface area, pore volume and average pore size) of Ca(OH)$_2$ samples were measured with a Micromeritics surface area analyzer which utilizes the BET low-temperature N$_2$ adsorption technique (ASAP 2000). Those properties, together with other physiochemical properties, are summarized in **Table 1**.

1.3 Product-distribution measuring method

A typical Ca(OH)$_2$ sample was calcined at 50 K.min^{-1} in a 125 cm^3.min^{-1} flow of N$_2$ up to 1023 K. Preliminary tests, based on continuous monitoring of the associated weight change, ensured complete calcination into CaO. This resulting calcine (CaO) was then sulfated at a predetermined temperature (823-1123 K) in a gas mixture (0.11-0.31 vol% SO$_2$, and 0-10 vol% O$_2$ in N$_2$) for specific periods (5-60 min). At the end of the predetermined sulfation period, both SO$_2$ and O$_2$ gases were quickly shut
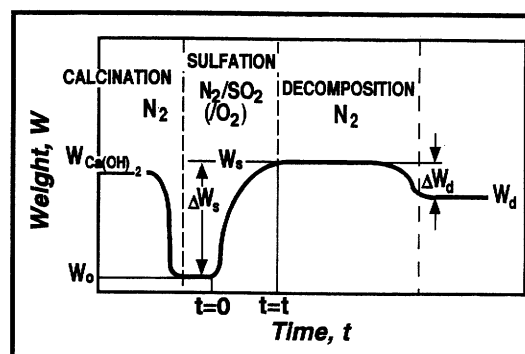
off, and the temperature was increased up to about 1123 K to allow for CaSO$_3$ decomposition (if it existed) into CaO and SO$_2$ according to reaction (2):

$$CaSO_3 \Rightarrow CaO + SO_2 \qquad (2)$$

In an N$_2$ atmosphere, it was found that CaSO$_3$ decomposed in the temperature range of 1033-1103 K. Thus, from the accompanied weight loss (ΔW_d), the weight percentage of CaSO$_3$ (y_1%) existing in the sulfation products (CaSO$_3$ and CaSO$_4$) can be determined as:

$$y_1\% = \frac{M_1}{M_1 - M_o}\frac{\Delta W_d}{W_s}100 = 1.875\frac{\Delta W_d}{W_s}100 \qquad (3)$$

where, M_1 is the molecular weight of CaSO$_3$, M_o is the molecular weight of CaO, and W_s is the weight of the sulfated sample at time = t.

Figure 1 shows typical TGA weight-time curves for the Ca(OH)$_2$ calcination, CaO sulfation and CaSO$_3$ decomposition reactions. It is important to notice that in all the conducted experiments, only small amounts of CaS were measured in the sulfation product (less than 8%). However, the amount of CaS that can be formed can not exceed 15 wt% in accordance with the stoichiometrics of reactions (5) or (6) shown later. Thus, equation (3) can be used only if CaS content in the sulfation product is negligible.

1.4 Experimental conditions reliability

Prior to a typical experiment, reliable and reproducible measurements were carefully ensured by maintaining a stable environment for the TGA microbalance. This was achieved by introducing a suitable amount of purge N$_2$ through the microbalance chamber to prevent SO$_2$ gas from diffusing into the chamber and, thus disturbing the microbalance recordings. The flow rate of the purge N$_2$ gas was, therefore, carefully set at 25 cm^3.min^{-1}.

Moreover, for the sake of obtaining accurate kinetic measurements, external mass and/or heat transfer were all eliminated by an appropriate total gas flow rate as well as a small, thin, and evenly distributed solid sample (2.5-3.5 mg). Accordingly, a total gas flow rate of 141 cm^3.min^{-1} was found to be high enough to eliminate external mass resistances, but low enough to guarantee stable microbalance recordings.

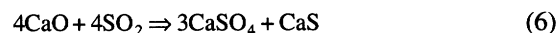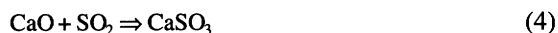**Table 2** CaSO$_3$ wt% (y_l%) in CaO/SO$_2$ sulfation products

T (K)	O$_2$ vol%	reaction time, t (min) 5 y_1%	10 y_1%	20 y_1%	40 y_1%	60 y_1%
823	0	78.3	49.5	30.7	18.5	11.6
823	2	52.3	17.1	4.5	1.2	0
823	5	51.1	13.7	7.1	0.8	0
873	0	70.1	41.3	24.2	9.3	3.2
873	2	27.6	7.3	2.1	0	0
873	5	25.4	6.8	1.4	0	0
923	0	58.4	49.1	33.7	16.5	6.3
923	2	13.7	9.3	3.8	0	0
923	5	11.2	10.7	2	0	0
973	0	41.9	25.2	13.2	4.2	1.2
973	2	5.1	0	0	0	0
973	5	4.2	0	0	0	0
1023	0	20.5	3.1	0	0	0
1023	2	0	0	0	0	0
1023	5	0	0	0	0	0
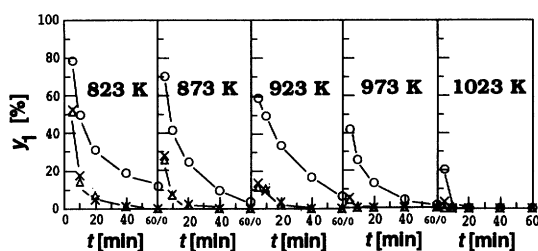
Fig. 2 Change in CaSO$_3$ wt% (y_l%) with reaction time during CaO reaction with 0.31 vol% SO$_2$ and O$_2$ concentrations of 0 (O), 2 (×), and 5 (△) vol%

Fig. 3 Change in CaSO$_3$ wt% (y_l%) with temperature for CaO reaction with 0.31 vol% SO$_2$ for 5 min
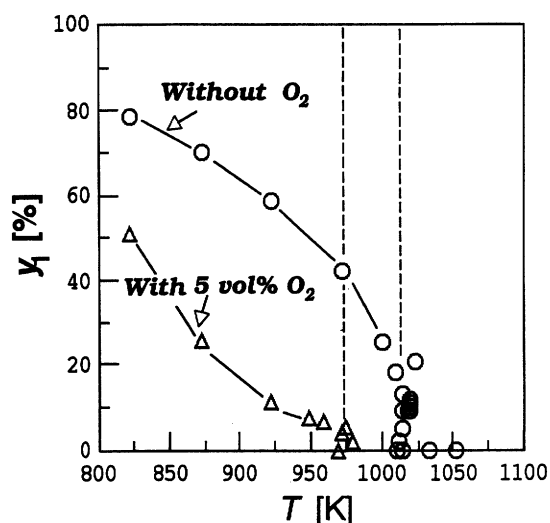
2 Theoretical considerations

At temperatures above 673 K, the reactions between CaO and SO$_2$ may proceed through different routes depending on the reaction temperature, O$_2$ concentration, and reaction time. In the absence of O$_2$, the reactions may involve:

$$CaO + SO_2 \Rightarrow CaSO_3 \qquad (4)$$

$$4CaO_3 \Rightarrow 3CaSO_4 + CaS \qquad (5)$$

$$4CaO + 4SO_2 \Rightarrow 3CaSO_4 + CaS \qquad (6)$$

In the presence of O$_2$, the reactions occurring between CaO and SO$_2$ can involve reaction (4) as well as reaction (7):

$$CaSO_3 + \tfrac{1}{2}O_2 \Rightarrow CaSO_4 \qquad (7)$$

The mechanisms by which CaO reacts with SO$_2$ still have not been clearly understood. In their investigations of CaO reaction with SO$_2$ at 1123 K, Fieldes *et al.* (1979) reported that limestone-derived CaO reacted directly with a SO$_3$ intermediate, formed via SO$_2$ oxidation, to form CaSO$_4$. Based on infrared analysis, Hatfield *et al.* (1970) showed that CaSO$_3$ was the major sulfation product below 913 K, and that at around 993 K, CaSO$_4$ was formed by CaSO$_3$ oxidation. They also stated that the decomposition reaction of CaSO$_3$ into CaO and SO$_2$, and its

disproportionation into CaS and CaSO$_4$ (via reaction (5)) started at around 993 K. In the presence of O$_2$ and above 1153 K, CaS can be oxidized into CaSO$_4$.

3 Results and discussion

3.1 Product distribution

The CaSO$_3$ weight percents (y_l%) existing in the sulfation products (CaSO$_3$ and CaSO$_4$) of CaO reaction with 0.31 vol% SO$_2$ at 0, 2, and 5 vol% O$_2$ under various temperatures (823-1023 K) are listed in **Table 2**. As can be observed, the product distribution depends on reaction temperature, time and O$_2$ concentration. **Figure 2** shows plots of the CaSO$_3$ weight percent (y_l%) against the reaction time, t, for samples sulfated at different temperatures. The amount of CaSO$_3$ was found to decrease remarkably with increasing reaction time and/or with the presence of O$_2$ for temperatures up to about 973 and 1023 K, respectively, with and without O$_2$. At certain values of O$_2$ concentration and reaction time, Fig. 2 also indicates a proportional decrease in CaSO$_3$ wt% with temperature increase.

Additional sulfation runs (measured after 5 min reaction of CaO with SO$_2$ in 0 and 5 vol% O$_2$) were required to detect the temperature region where CaSO$_3$ is present in significant amounts as depicted in **Fig. 3**. In this figure, the weight percentage of CaSO$_3$ (y_l%) was measured at different temperatures for reactions conducted under both O$_2$-free and 5 vol% O$_2$-containing conditions. Under O$_2$-containing and O$_2$-free conditions, the highest temperatures at which CaSO$_3$ existed were determined as 973 and 1015 K, respectively. In the prevailing atmosphere, two dotted lines were vertically drawn through the 973 and 1015 K temperature points to represent the limits (ultimate temperatures) where CaSO$_3$ was present (termed as CaSO$_3$ stability limits). Accordingly, the region of temperatures lower than the stability limits, where CaSO$_3$ exists, is
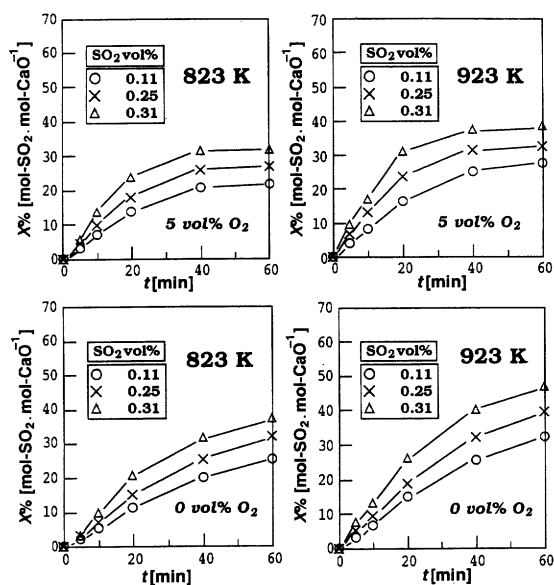
Fig. 4a Total conversion of CaO (X)-time progress at temperatures within $CaSO_3$ stability limits

Fig. 4b Total conversion of CaO (X)-time progress at temperatures beyond $CaSO_3$ stability limits

defined as "within $CaSO_3$ stability limits", whereas that region of temperatures higher than the stability limits is defined as "beyond $CaSO_3$ stability limits".

3.2 Effect of SO_2 and O_2 concentrations

i) WITHIN $CaSO_3$ STABILITY LIMITS

Figure 4a shows the CaO total conversion changes with reaction time (X-t curves) at 823 and 923 K, and different SO_2 concentrations (0.11, 0.25 and 0.31 vol%). As a general observation, in the presence of O_2, the initial reaction rates are higher than those without O_2 corresponding to the same reaction conditions (temperature and SO_2 concentration). This may be attributed to the difference between their respective reaction mechanisms. Thus, the initially slow O_2-free reaction is presumed to proceed according to reaction (4). This presumption was experimentally confirmed by the product distribution results which showed that $CaSO_3$ was initially the main (if not the only) sulfation product (for example, sulfation products contained around 78% within 5 min reaction at 823 K (Table 2)). Then, with the passage of time, $CaSO_3$ was converted into $CaSO_4$ and CaS according to the disproportionation reaction (5) and/or the CaO-SO_2 direct reaction (6). Accordingly, the weight fraction of $CaSO_3$ (y_j) was decreasing with time elapse.

In the presence of O_2, the $CaSO_3$ (formed by reaction (4)) was rapidly oxidized into $CaSO_4$ in accordance with reaction (7). This oxidation reaction was proven to be initially very fast, but progressively became slower and, finally, almost completely blocked (Van-Houte and Delmon, 1979). One reason for this blocking is most probably the substantial increase in the molar volume of particles as oxidation proceeds (from 42.0 to 52.0 $cm^3.mol^{-1}$ as $CaSO_3$ is transformed into $CaSO_4$), and thus the available openings (pores) in $CaSO_3$ are rapidly blocked with the forming impervious layer of $CaSO_4$ preventing SO_2 from diffusing further. Furthermore, at higher temperatures, the

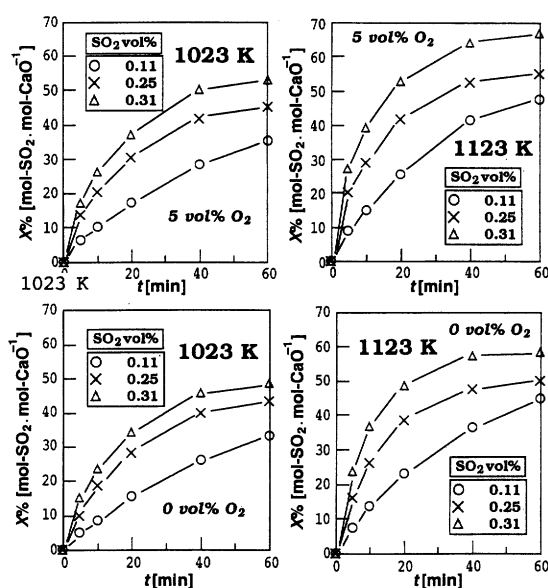blocking effect appears more dominant as a result of the initially higher oxidation rate causing a thicker product layer with stronger diffusion limitations. In light of these considerations, Fig. 4a shows that the reaction proceeds faster at the beginning (compared to O_2-free reaction), but terminates with noticeable drops in reactivity after reaching certain conversions, depending on the reaction temperature as well as on the gases concentrations. After 1 h reaction and at 0.31 vol% SO_2, for instance, the conversions dropped by about 14 and 18%, respectively, at 823 and 923 K.

ii) BEYOND $CaSO_3$ STABILITY LIMITS

Figure 4b shows X-t curves at 1023 and 1123 K, and different SO_2 concentrations (0.11, 0.25 and 0.31 vol%). Similar to data at temperatures within the stability limits, with and without O_2 presence, both the initial reaction rates and final conversions (capacities) were increased with SO_2 concentration. At similar values of temperature and SO_2 concentration, both the initial reaction rates and capacities increased with the presence of O_2. In this high temperature region, $CaSO_3$ was thermally unstable and immediately transformed into $CaSO_4$ and CaS. This transformation might occur directly by disproportionation and/or oxidation reactions (reaction (5) and/or reaction (6)), or through the CaO/SO_2 reaction (6) following $CaSO_3$ decomposition into CaO and SO_2.

The reason that the O_2-containing sulfation had higher conversions than those of O_2-free sulfation (Fig. 4b) might be attributed to the additional contribution for sulfur capture by the oxidation reaction, as it takes place only with O_2 presence. Another reason might be due to the different pore characteristics, as will be discussed later.

3.3 Kinetic parameters

i) REACTION ORDER WITH RESPECT TO SO_2

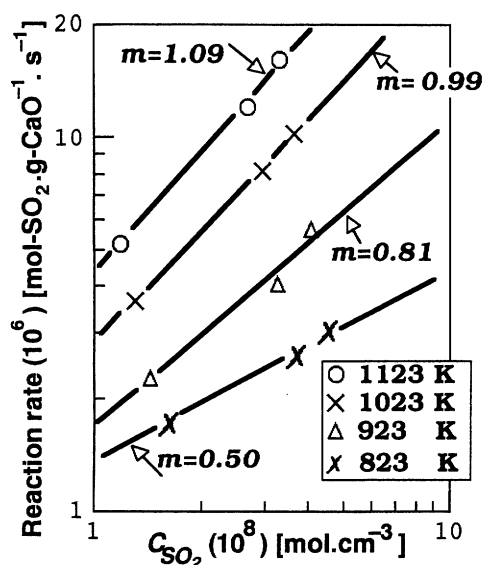Throughout the entire temperature range studied (823-1123 K), the initial reaction rates were determined by

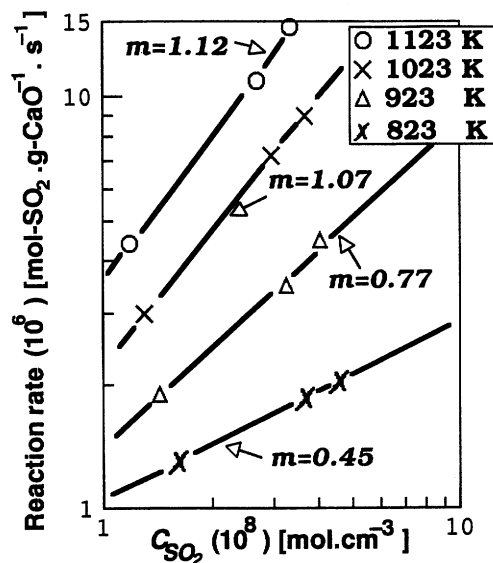Fig. 5a Effect of SO_2 on sulfation of CaO at 5 vol% O_2 and various temperatures

Fig. 6 Total conversion of CaO (X)-time progress at different temperatures and different O_2 concentrations

Fig. 5b Effect of SO_2 on sulfation of CaO at 0 vol% O_2 and various temperatures

Fig. 7 Effect of O_2 concentration on CaO sulfation at 0.31 vol% SO_2 and various temperatures

taking the slope of Figs 4a and 4b at $X = 0.0$. These initial reaction rates with and without O_2 were log-log plotted against SO_2 concentration (C_{SO2}) as shown in **Figs 5a** and **5b**, respectively. The reaction order in SO_2 concentration was, thus, determined as the slope (m) of the lines best fitted with the least-squares method. Accordingly, the reaction order (in SO_2) was found to increase with temperature below the stability limits. This is qualitatively in good agreement with the experimental and modeling results shown by Dam-Johansen (1987), and Dam-Johansen and Østergaard (1991). The reaction order, with and without O_2, increased from 0.50 to 0.81 and from 0.45 to 0.77, respectively, when increasing the temperature from 823 to 923 K. However, beyond the stability limits, the sulfation reaction order with respect to SO_2 tends to approach unity,
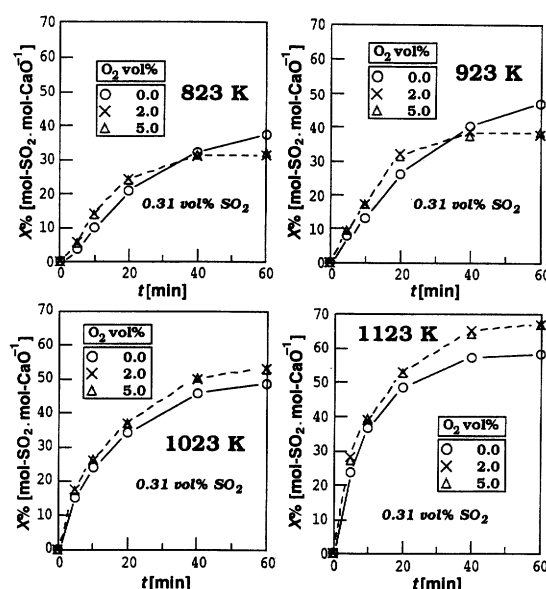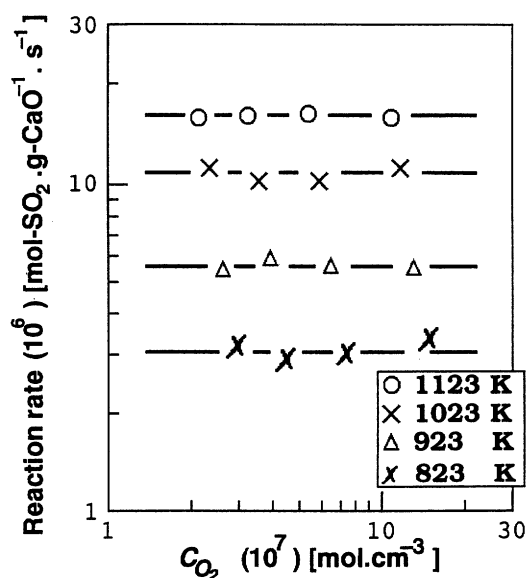
independent of O_2 presence.

ii) **REACTION ORDER WITH RESPECT TO O_2**

The effect of O_2 concentration (0, 2 and 5 vol%) on the CaO reactivity at 0.31 vol% SO_2 and 823-1123 K is shown in **Fig. 6**. Within $CaSO_3$ stability limits (823 and 923 K), increasing O_2 concentration from 0 to 2 vol% increased the initial reaction rate, but the capacity was decreased. No effect on the initial reaction rates, nor the capacities, was observed upon increasing O_2 concentration above 2 vol%. At 1023 and 1123 K (beyond $CaSO_3$ stability limits), the increase of O_2 concentration from 0 to 2 vol% increased both the initial reaction rates and capacities. However, in all other reaction temperatures investigated, increasing O_2 concentration from 2 to 10 vol% had no effect on the reac-
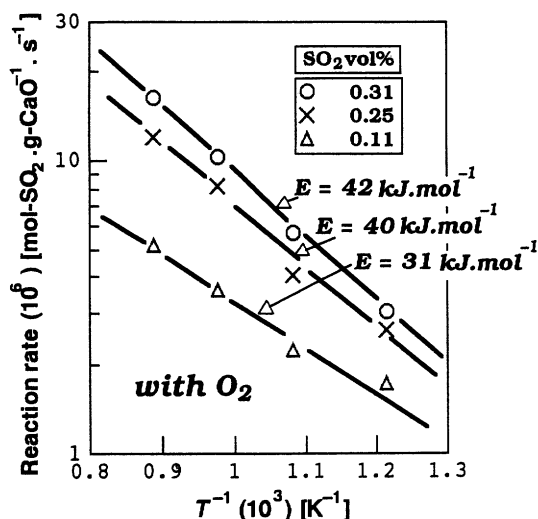
Fig. 8a Arrhenius plots for CaO reaction with SO_2 (0.11, 0.25, & 0.31 vol%) and 5 vol% O_2
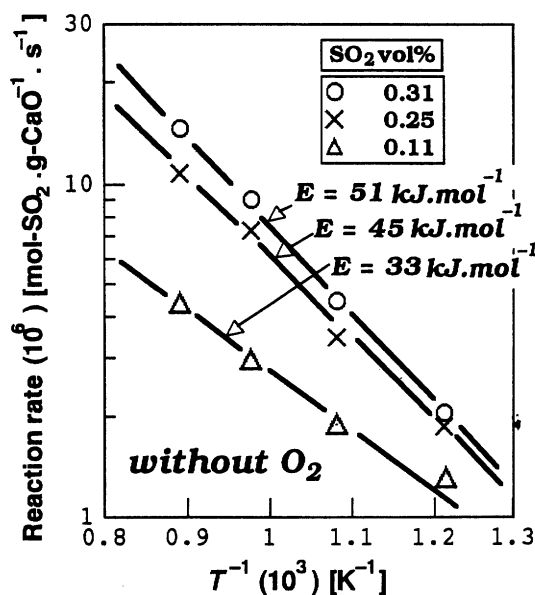

Fig. 8b Arrhenius plots for CaO reaction with SO_2 (0.11, 0.25, & 0.31 vol%) and 0 vol% O_2

tivity of CaO with SO_2 as **Fig. 7** shows.

iii)   ACTIVATION ENERGY

Figures 8a and **8b** show that the temperature dependency of the reaction rate could be correlated by the Arrhenius equation with an apparent activation energy (E) ranging from 31 to 51 kJ.mol^{-1}. These values compare fairly well with those estimated by Borgwardt (1970), and Wen and Ishida (1973).

3.4   Pore-structural properties

In this section, the evolution of pore specific surface area (Sa) and volume (Va) during the CaO-SO_2 reaction was measured at different conversion degrees. The influence of the reaction temperature and O_2 concentration on Sa and Va changes was also determined.

a)   SPECIFIC SURFACE AREA (Sa)

Figure 9 illustrates the deterioration of pore specific
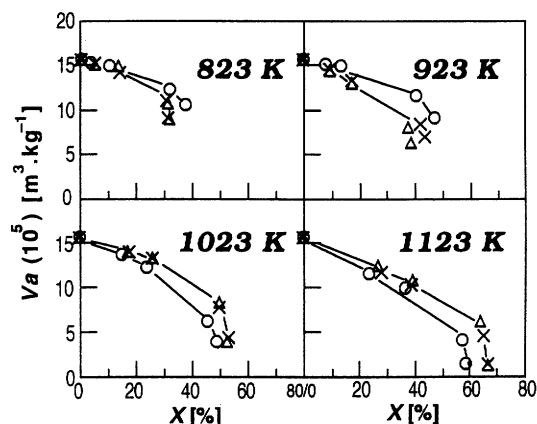

Fig. 9 Specific surface area (Sa) change with CaO conversion at different temperatures and O_2 concentrations of 0 (○), 2 (×), and 5 (△) vol%

surface area (Sa) with CaO conversion at different temperatures and O_2 concentrations. All sulfation runs were performed in a 0.31 vol% SO_2-containing gas mixture using CaO calcine of the same initial surface area (33.1 × 10^3 m^2.kg^{-1}). As sulfation proceeded, Sa values began to decline at higher rates with temperature increase. No appreciable influence of increasing O_2 concentration from 2 to 5 vol% was observed. It is interesting, however, to notice that the presence of O_2 had an opposite effect on Sa declination within and beyond the $CaSO_3$ stability limits. Within the stability limits (such as at 823 and 923 K), it can be seen that Sa declination proceeds more slowly in the absence of O_2. This, accordingly, allowed for higher conversion of CaO. After a 1 h reaction at 823 K, for example, conversions of 31-32% and 37% could be attained, with and without O_2 presence, respectively.

On the other hand, in the absence of O_2 and beyond the stability limits (such as at 1023 and 1123 K), the Sa decrease proceeded faster than that with O_2, particularly at low conversion levels. Beyond higher conversion degrees (> ~40%), however, Sa seemed to decay at a similar rate, irrespective of O_2 presence. Figure 9 also indicates that Sa values were mostly lost in the initial conversions (below around 15%).

b)   SPECIFIC PORE VOLUME (Va)

Figure 10 shows Va values measured at different conversion degrees, O_2 concentrations (0, 2, and 5 vol%) and temperatures (823-1123 K). As seen, the higher the temperature, the faster the decline in Va all. Another observation is that, unlike reduction in Sa, reduction in Va proceeded faster at higher conversion levels. The presence of O_2, within stability limits, speeded up Va loss and eventually led to lower conversions compared to those without O_2. Beyond stability limits, the slower rate of Va decline, in O_2 presence, allowed for higher conversions than those without O_2. After a 1 h reaction at 1123 K, for example, conversions of around 67 and 58% were found with and without O_2 presence, respectively.

Thus, for highly improved SO_2 emission control, it is favorable if Sa and Va values are not only large, but also
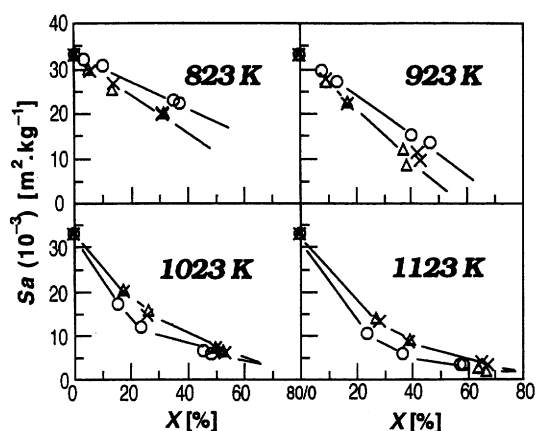
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Fig. 10 Specific pore volume (*Va*) change with CaO conversion at different temperatures and O_2 concentrations of 0 (O), 2 (×), and 5 (△) vol%

of lower declining rate as sulfation progresses. Owing to the relatively low reaction rate, it may be noticed that at temperatures below 1023 K, available pores are slowly accommodated with sulfation products ($CaSO_3$ and $CaSO_4$). Consequently, the slower decline in *Va* left an appreciable porosity within the partially sulfated particles. This may, qualitatively, indicate that lesser importance of the pore or product-layer diffusion limitations compared to chemical reaction. Therefore, for longer reaction times, further SO_2 capture might be achieved even at a much slower rate. On the contrary, at higher temperatures, the faster CaO-SO_2 reaction immediately fills nearly all the pores with an impervious layer of $CaSO_4$, thus impeding SO_2 gas from further penetration. The reaction becomes finally under the growing product ($CaSO_4$)-layer diffusion limitations, as was concluded by previous investigators (Pigford and Sliger, 1973; Sotirchos and Yu, 1985). Accordingly, the sulfation reaction virtually ceases with incomplete conversion at *Va* values approaching zero. In this work, incomplete conversion (58-67%) at 1123 K may be ascribed to the small pore plugging phenomenon. Details on this phenomenon, regarding the CaO-SO_2-O_2 reaction system, are addressed in our previously published article (Al-Shawabkeh et al., 1994a).

Conclusions

The product distribution of the CaO-SO_2 reaction, mainly $CaSO_3$ and $CaSO_4$, varied with reaction time, temperature and O_2 presence. With or without the presence of O_2, $CaSO_3$ was found to be thermally stable at temperatures below 973 or 1015 K, respectively. Thus, depending on whether the reaction temperature is within or beyond $CaSO_3$ stability limits, O_2 influence as well as pore properties differ as may follow:

a)   Within $CaSO_3$ stability limits

1) The mole fraction of $CaSO_3$ was observed to decrease with O_2 presence, and/or with increasing the reaction time and/or temperature.

2) The presence of O_2 resulted in suppression of the SO_2-

sorption capacity, although the initial sulfation rate was higher than that without O_2.

3) Irrespective of O_2 presence, the reaction order with respect to SO_2 increased from 0.5 to 0.8 with increasing temperature from 823 to 923 K, respectively.

4) Pore specific surface area and volume were reduced by the presence of O_2.

b)   Beyond $CaSO_3$ stability limits

1) Independent of O_2 presence, reaction time and temperature, $CaSO_4$ was detected as the only sulfation product in the temperature range between 1015 and 1123 K.

2) Improving both the pore specific surface area and volume in O_2 presence led to higher initial sulfation rate and sorption capacity as well.

3) Regardless of O_2 existence, the reaction order in SO_2 remained close to unity.

Throughout all the tested temperature range (823-1123 K), increasing O_2 concentration from 2 to 10 vol% had no effect on the reactivity of CaO with SO_2. An activation energy, *E*, between 31 to 51 kJ.mol^{-1} could correlate the temperature dependency of the CaO-SO_2 reaction system.

Nomenclature

C_{O2}	= O_2 in phase	[mol·cm^{-3}]
C_{SO2}	= SO_2 in phase	[mol·cm^{-3}]
d_p	= mass mean diameter	[μm]
E	= apparent activation energy	[J·mol^{-1}]
M_o	= CaO molecular weight	[kg·mol^{-1}]
M_I	= $CaSO_3$ molecular weight	[kg·mol^{-1}]
P_{O2}	= partial pressure of oxygen	[Pa]
P_{SO2}	= partial pressure of sulfur dioxide	[Pa]
r_p	= average pore radius	[nm]
Sa	= specific surface area	[m^2·kg^{-1}]
t	= exposure time	[min]
T	= reaction temperature (absolute)	[K]
Va	= specific pore volume	[m^3·kg^{-1}]
W_s	= weight of sulfated sample at time = t	[kg]
X	= total CaO conversion into $CaSO_3$ and $CaSO_4$ [mol-SO_2·mol-CaO^{-1}]	
y_I	= weight percentage of $CaSO_3$ present in sulfation products	[%]
ΔW_d	= weight loss upon $CaSO_3$ decomposition	[kg]
ρ	= particle density	[kg·m^{-3}]

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