

SO₂ retention at low temperatures by Ca(OH)₂-derived CaO: a model for CaO regeneration

J. García-Martínez, A. Bueno-López, A. García-García, A. Linares-Solano*

Department of Inorganic Chemistry, University of Alicante, Carretera San Vicente del Raspeig, 03690 Alicante, Spain

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Abstract

The retention of SO₂ by Ca(OH)₂-derived CaO has been studied at 573 K. The thermal treatment of Ca(OH)₂ forms CaO sorbents with high activity to retain SO₂. At the temperature of 573 K, it has been proved that SO₂ interacts with CaO to form a surface CaSO₃ specie.

The regeneration process by thermal decomposition of CaSO₃, giving SO₂ and CaO, has been examined using techniques such as in situ FTIR and in situ XRD. In addition, CO₂ chemisorption and SO₂ sorption and sorbent regeneration was evaluated by thermogravimetry.

The thermal regeneration process used to decompose CaSO₃ causes an important loss in the SO₂ retention capacity of the sorbent. Using several experimental procedures, a series of reactions have been analysed (Ca(OH)₂ decomposition, formation of superficial CaSO₃, change from surface to bulk CaSO₃ and CaSO₃ decomposition) and an insight into the regeneration process has been obtained.

The decrease in SO₂ retention, following the thermal regeneration step, is due to both an increase in the particle size and the conversion of CaSO₃ into CaSO₄ and CaS (CaSO₃ disproportionation) upon heat treatment. The increase in the particle size is responsible for about 88% of the loss of activity, whereas CaSO₃ disproportionation explains a 12% of loss. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: SO₂ retention; Calcium oxide; CaO regeneration

1. Introduction

Stricter government regulations on pollutant emissions and the need to improve process efficiency have led to the development of advanced cleaning systems. The technologies for the control of SO₂ emissions cover control in all three stages of the combustion cycle: prior to combustion (by coal cleaning), during combustion (by use of SO₂ sorbents in fluidised bed combustion (FBC)), and after combustion (by flue gas desulphurisation (FGD)) [1–5].

Both FGD (wet and dry, regenerable and non-regenerable) and FBC processes provide consistent removal of SO₂ from coal combustion; however, large amounts of solid wastes are generated because of difficulties with sorbent regeneration. An alternative would be to find a desulphurisation route that allows both the regeneration of the sorbent and the recovery of the sorbent-bound sulphur as a valuable product, sulphur dioxide [6]. In this sense, the SO₂ capture by calcium-based sorbents (mainly CaCO₃ and Ca(OH)₂-based sorbents) was investigated at low temperatures (≤ 573 K) with the objective of favouring CaSO₃ formation [7–11]. The thermal decomposition of this compound

(yielding CaO and SO₂) would enable sorbent reutilisation and SO₂ recovery. In fact, at temperatures slightly higher than 473 K, CaSO₃ is formed [7–12] and there is experimental evidence that only the external active area of CaO is responsible for the SO₂ uptake, forming surface sulphite [9–11,13]. Interestingly, calcium sulphite thermally decomposes to SO₂ and CaO at a temperature >973 K [7,10–12]. Consequently, the SO₂ retention by CaO to form CaSO₃ is theoretically reversible, and provides a possible route for a regenerative technology.

Unfortunately, previous studies carried out in our laboratories, have demonstrated that the regeneration treatment in N₂ produces an important loss in the subsequent SO₂ retention capacity [6,11]. Several causes have been proposed to explain this deactivation: (i) the increase of the CaO particle size due to the thermal treatment; (ii) the CaO sintering–agglomeration due to the presence of CaSO₃, formed during the CaO/SO₂ interaction; (iii) the possible conversion of CaSO₃ into CaSO₄ and CaS, which are species non-regenerable under the conditions tested [7,11,14].

The present paper examines the SO₂ retention by Ca(OH)₂-derived CaO at 573 K, to form mostly CaSO₃, and the regeneration process by thermal treatment at higher temperatures. In addition, the paper analyses the possible causes that explain the decrease in SO₂ adsorption after the

* Corresponding author. Tel.: +34-96-590-3545; fax: +34-96-590-3454.
E-mail address: linares@ua.es (A. Linares-Solano).

regeneration. A model that explains the regeneration of the sorbent is proposed.

2. Experimental

Commercially available $\text{Ca}(\text{OH})_2$ (supplied by PANREAC, 95 wt% purity) has been used. To characterise the CaO, derived from $\text{Ca}(\text{OH})_2$, during and after the steps involved in a cycle of SO_2 retention and subsequent regeneration, the following techniques have been used:

(a) *In situ FTIR*: The infrared experiments have been performed with a spectrophotometer FTIR Mattson, model Infinit MI60, with a diffuse reflectance accessory Model Collector of Spectra Tech. The controlled environment chamber allows the control of the temperature during the experiments, as well as the control of different reactive gases (SO_2 in this case), and the possibility of working under vacuum or under a controlled gas flow.

(b) *Thermogravimetry*: The thermobalance used is a simultaneous TG-DTA (Stanton-Redcroft Series 780). Two different sets of experiments have been performed with this equipment:

(b1) *Carbon dioxide chemisorption at 573 K*, to determine the CaO active surface area of the samples (defined as the CaO area that, exposed to CO_2 , chemisorbs it) following the experimental procedure described elsewhere [15].

(b2) *SO_2 retention experiments, involving one or two cycles*. Isothermal reaction experiments on SO_2 retention at 573 K were performed in the thermobalance as follows, using an SO_2 - N_2 mixture (0.3 vol% SO_2):

- 2.1. The $\text{Ca}(\text{OH})_2$ sample was heated in a 90 ml/min flow of N_2 at a rate of 20 K/min to 723 K to decompose the calcium hydroxide into calcium oxide.
- 2.2. The sample was then cooled at 20 K/min to the reaction temperature (573 K).
- 2.3. The SO_2/N_2 reaction mixture was contacted with the sample for 2 h.
- 2.4. The saturated sample was heated at 20 K/min, in N_2 flow, at 773 or 1153 K to regenerate the sorbent.
- 2.5. The treated sample was again put in contact with the SO_2/N_2 mixture until saturation of the sorbent.

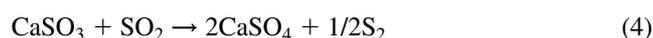
In addition, $\text{Ca}(\text{OH})_2$ decomposition (step 1) was analysed with a combined TG-DSC-MS. The TG-DSC used is a TA Instruments (model SDT 2960) and the MS a Balzers Instruments (model GSD 300 T3).

(c) *XRD in situ*: The regeneration step in N_2 after SO_2 retention has been analysed in situ by X-Ray diffraction provided with a high temperature chamber. The apparatus is a Rigaku D/max III C Diffractometer with a radiation source $\text{Cu}(\alpha)$ (50 kV, 30 mA).

3. Results and discussion

3.1. IR study

According to thermodynamic 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 [7–9,14,16]. In the absence of oxygen, the following reactions can be involved [7,11,14,16]:



In the presence of O_2 , the reactions occurring between CaO and SO_2 can involve reactions (1)–(4) as well as reaction (5) [7,11,14,16]:



Because of our interest in the regeneration step, the desired reaction product is CaSO_3 , which is potentially regenerable by thermal treatment decomposing around 973–1073 K according to the reaction [7–12]:



Other species that can be involved (CaSO_4 and CaS) need much higher temperatures to be decomposed, as described in the literature, (1473 K or higher for the case of CaSO_4 [14]).

Our in situ infrared study (see Fig. 1) has been performed at different temperatures to analyse the co-existence of other sulphur species formed through the above mentioned routes (2), (3) or (4). The figure shows the IR spectra of $\text{Ca}(\text{OH})_2$, of CaO (formed by thermal decomposition of $\text{Ca}(\text{OH})_2$ up to 723 K) and those of CaO submitted to SO_2 flow at different temperatures (573, 673 and 773 K). The spectrum (a) corresponding to the fresh sorbent, shows the band assigned to OH of $\text{Ca}(\text{OH})_2$, around 3640 cm^{-1} and the two bands corresponding to calcium carbonate (875 and 1480 cm^{-1} , respectively). These two bands indicate, as it is well known, that a degree of carbonation occurs when the sample is exposed to the air during handling. Spectrum (b) corresponds to calcium hydroxide after a heat treatment at 723 K in He. An important decrease in the hydroxide assigned band is shown, confirming the water loss as a consequence of calcium hydroxide decomposition to CaO. According to Nakamoto et al. [17], the unique band that could be assigned to CaO would be at 650 cm^{-1} , (but the equipment used could only record from 800 to 4000 cm^{-1}). The band at 875 cm^{-1} and the broad band at 1400 – 1500 cm^{-1} , can be ascribed to the presence of some CaCO_3 , which remains after the thermal treatment carried out (723 K), because

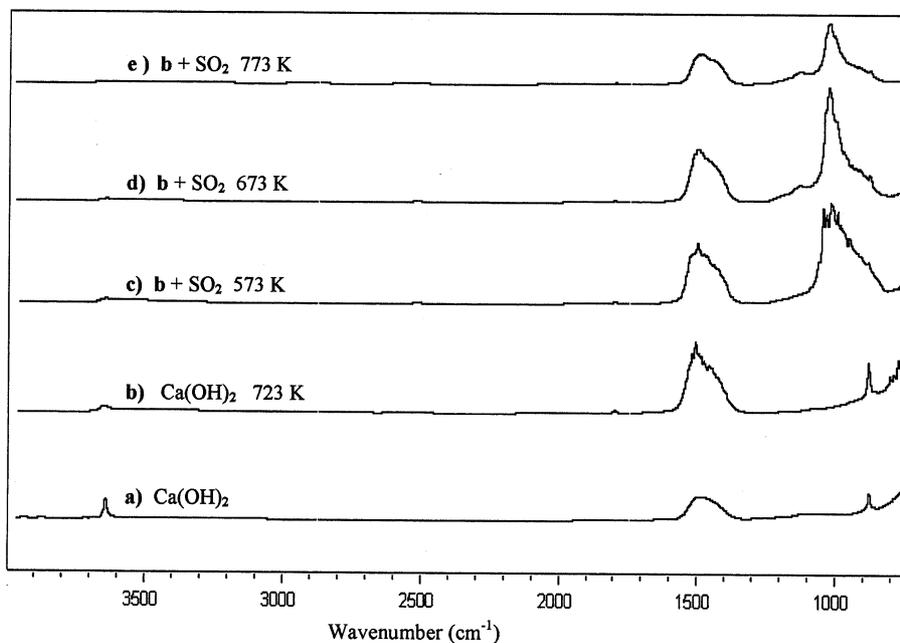


Fig. 1. In situ FTIR spectra of Ca(OH)₂ and Ca(OH)₂-derived CaO samples after different treatments.

carbonate decomposition occurs at higher temperatures, about 1098 K [18]. Also, undecomposed Ca(OH)₂ can be present. Fig. 2 shows the corresponding TG–MS profile of the Ca(OH)₂ thermal decomposition process to corroborate the band assignment in the spectra. From these profiles, two important points have been checked: the decomposition of Ca(OH)₂, evolving H₂O (*m/z* 18) and the presence of a certain amount of CaCO₃ in the original sample, manifested

by a slight weight loss at 923 K in the thermogravimetric curve.

Spectra (c)–(e) show the products of the reaction between CaO and SO₂ (0.45 vol% in N₂) for the temperatures 573, 673 and 773 K. The broad band around 1000 cm⁻¹, that appears from 573 K is assigned to the S–O stretching, suggesting the appearance of CaSO₃, formed by reaction (1) [7,11,14,16].

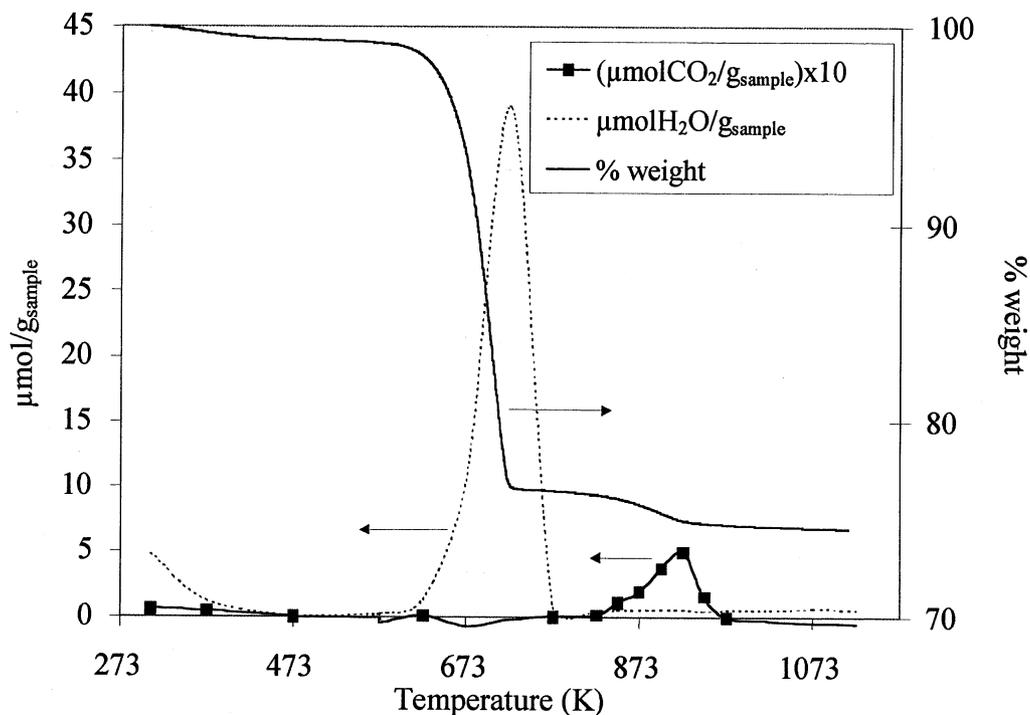


Fig. 2. TG–MS profiles of Ca(OH)₂ decomposition in N₂.

Table 1
Data related to SO₂ retention experiments at 573 K

	mg SO ₂ ret./g CaO (after step 3), first cycle	SO ₂ /CaO molar ratio	mg SO ₂ ret./g CaO (after step 5), second cycle	SO ₂ /CaO molar ratio
Programme 1	250.6	0.219	42.3	0.037
Programme 2	–	–	122.2	0.107

The spectra (d) and (e) show a decrease in the intensity of the band located at 1000 cm⁻¹ as well as the appearance of a new band at 1100 cm⁻¹ characteristic of sulphate. The absence of the sulphate band at 573 K, confirms that at this temperature the only species formed, due to SO₂ and CaO interaction is calcium sulphite. As the temperature is increased to 673 and 773 K, further reactions can occur with calcium sulphate formation involving mainly routes (2) or (3). The formation of elemental sulphur through route (4), at any of the temperatures used, has not been detected. As a summary, the main feature of this study is the assessment of the formation of CaSO₃ as the unique sulphur-containing compound, if the temperature is not higher than 573 K. This is of great interest because sulphite is potentially regenerable [7,10,11,14,16].

These findings are in good agreement with those reported by Palmer et al. for an in situ FTIR characterisation of sulphur–oxygen species resulting from reaction of SO₂ with CaCO₃, who found sulphate formation above 773 K [19].

3.2. Study of the regeneration process

CaSO₃ has been confirmed as the only product of CaO–SO₂ reaction at 573 K. Afterwards, the SO₂ retention capacity has been tested in two cycles of SO₂ adsorption to investigate the regeneration step and the loss in SO₂ retention capacity reported elsewhere [6,11]. Two sets of experiments have been performed: one of them following the programme analysis of SO₂ retention, as described in Section 2, (Programme 1) and the other without SO₂, i.e. maintaining N₂ in the third and fourth steps (Programme 2). The comparison of the results obtained with both programmes allows to check the influence of SO₂. Table 1 shows the amount of SO₂ retained by the sample during the first cycle and after the regeneration step (for both sets of experiments). It is clear that the heat treatment to decompose the CaSO₃ formed causes an important loss of SO₂ retention capacity, probably due to a loss of surface area process of the calcium compound.

To assess if this loss is due to the presence of CaSO₃, or only to CaO, the results of Programme 2 are discussed.

It can be observed that the adsorption corresponding to the second cycle for Programme 2 (with N₂ exposure in the step 3) is higher than that monitored for Programme 1 (with SO₂ exposure in the step 3). Therefore, part of the decrease in the SO₂ retention capacity is due to contribution of loss of CaO surface area originated by the thermal treatment at

1153 K (250 mg/g versus 122 mg/g), and part (122 mg/g versus 42 mg/g) has to be due to other causes related to the formation of CaSO₃ and its subsequent decomposition. Therefore, two factors seem to affect the sorption capacity of the regenerated sorbent:

1. The decomposition of CaSO₃ seems to favour the decrease of active surface area (defined as the CaO area that is able to capture SO₂) because the presence of SO₂ can favour the loss of CaO surface area. This was also found in the presence of CO₂ [20].
2. CaSO₃ can also undergo conversion to CaSO₄ and CaS, as described in reaction (2) [7,11,14,16], which will not regenerate CaO under the conditions used.

3.2.1. Increase of CaO particle size due to the presence of CaSO₃

To assess the contribution of the two above-mentioned factors, the increase in the CaO particle size due to the presence of CaSO₃ was analysed from the assessment of the active surface area of CaO, after different steps of SO₂ retention.

A fundamental characteristic of a calcium sorbent is its active surface area. This property can be characterised by CO₂ chemisorption at 573 K as described in the literature [15,21,22]. At this temperature, CO₂ is chemisorbed onto the sorbents according to the reaction:



After steps 2 (before regeneration) and 4 (after regeneration) (described in Section 2) the CO₂ chemisorption values of the sorbent were 220.7 mg CO₂ and 27.5 mg CO₂/g CaO, respectively. From these chemisorption values, the CaO dispersion can be assessed by dividing the number of moles of superficial CaO (deduced from CO₂ chemisorption) by the number of moles of CaO present. Thus, the dispersion values determined were 0.281 and 0.035 mol CaO_(sup)/mol CaO, respectively.

From the dispersion values, the CaO particle size can be obtained assuming a space model consisting of a cube with five faces exposed to the gas atmosphere (the sixth one is attached to the carbon support) by using the following equation [23]:

$$D = 5M/d\rho AN_A \quad (8)$$

where D , M , ρ and A are the particle size, the molecular

Table 2
Estimations of dispersion, chemical area and particle size from CO₂ chemisorption at 573 K

	Dispersion	Chemical area (m ² /g)	Particle size (Å)
Sorbent before regeneration	0.281	348.5	43.7
Sorbent after regeneration	0.035	43.4	354.3

weight, the density and the molecule area of CaO, respectively, and N_A is the Avogadro number.

On the other hand, CO₂ chemisorption allows the determination of the area of the CaO, which is chemically active by the Eq. (9).

$$\text{Active area (m}^2\text{/g)} \quad (9)$$

$$= 2 * (\text{CaO}_{(\text{sup})}/\text{CaO}) * N_A * (2.401 \times 10^{-10})^2/M$$

where 2.401×10^{-10} is the interionic distance (in Å) between the atoms of Ca and O in the structure attributed to CaO (NaCl type lattices) [24,25] and CaO_{sup} is the number of mol of CaO in surface equivalent to the mol of CO₂ chemisorbed. In this equation, the term $(\text{CaO}_{(\text{sup})}/\text{CaO})$ (mol/mol) corresponds to the dispersion. Table 2 shows the dispersion, chemical area and particle size of the sorbent before and after the regeneration. It can be seen that the regeneration step produces an important decrease in the dispersion and active area, and hence significant increase in particle size.

Comparing the values in Table 2 with others reported in the literature, we have to mention that Ca(OH)₂ heat-treated up to 723 K, gives CaO with a higher dispersion, higher area and lower particle size than any of the limestones, analysed in a previous study, which were heat-treated up to 1173 K [10,14]. In the study mentioned, the particle size and the dispersion of the CaO derived from eight limestones, ranged from 90 to 390 Å and from 0.204 to 0.13, respectively. These numbers agree with the observation that in high-temperature sorbent injection applications, the calcium oxide sorbent derived from hydrated limes (Ca(OH)₂) presents higher activity than those derived from limestones (CaCO₃) [26] because they also have higher active surface area.

Unfortunately, the data presented in Table 2 demonstrate that the thermal regeneration process (up to 1153 K) causes an important increase of the CaO particle size (from 44.1 to 354.3 Å) and a loss of active surface area of about 90%. It is clear that this important phenomenon has to be related to the presence and decomposition of CaSO₃.

In an attempt to explain the important increase of the CaO particle size caused by the presence of CaSO₃, a quantitative study of the regeneration step was performed. Fig. 3 presents the SO₂ profiles during the regeneration step after SO₂ retention at 573 K as a function of time. The decomposition of the CaSO₃ formed at 573 K presents two well differentiated peaks with a 28% of the CaSO₃ at about 1023 K and a 78% at about 1123 K. The appearance of two different peaks suggests the presence of both surface

an bulk CaSO₃. Two possibilities can explain the presence of these two peaks: (i) the SO₂ retention step might give both surface and bulk CaSO₃ and (ii) a transformation of surface into bulk CaSO₃ may occur during the own thermal regeneration treatment up to 1153 K.

To identify which of these two possibilities is responsible for the appearance of CaSO₃ bulk, additional TG experiments were carried out. The SO₂ retention step at 573 K was extended until no weight increase was observed. In this period, the amount of SO₂ adsorbed was of 321.2 mg SO₂/g CaO, corresponding to 0.281 mol SO₂/mol CaO (the same value corresponding to dispersion, see Table 2). This means that the same number of SO₂ and CO₂ mol is adsorbed per CaO mol. As it is known that CO₂ chemisorption at 573 K only yields surface CaCO₃ [15,21,22], we propose that the formation of CaSO₃ is also restricted to a surface process. Therefore, the transition of part of surface into bulk CaSO₃ has occurred during the thermal treatment up to 1153 K of the regeneration process.

To understand how this transition of CaSO₃ surface into bulk has been produced during the regeneration process, different sets of experiments have been carried out. The possible mechanism of ionic diffusion of SO₂ into the interior of the particle previously mentioned in the literature [14], does not seem our case. In fact, a new set of experiments have been performed (SO₂ retention at 573 K, regeneration in N₂ up to 773 K* for 10 min or for 5 h, second SO₂ retention at 573 K). This regeneration temperature of 773 K has been chosen to avoid concurrent SO₂ emission from CaSO₃ decomposition. If a mechanism of ionic diffusion of SO₂ into the interior of the CaO particle occurs before the CaSO₃ decomposition, a fraction of CaO surface would leave new available surface to retain SO₂ in the second retention. It has been observed that only an 8% of the whole CaO surface is available for a new retention process. Therefore, an ionic diffusion process cannot account for the transition of the surface to the bulk compound in which a 72% of the whole CaSO₃ is transformed into bulk compound.

The most reasonable hypothesis to explain this CaSO₃ surface–bulk transition is that the particle size increases very much after the regeneration process (due to a sintering–agglomeration process), in fact a decrease of an 88% in active surface area is observed. This process of particle size increase, that seems to occur during the CaSO₃ decomposition with emission of SO₂, (at temperatures higher than 773 K), converts part of the surface CaSO₃ into bulk.

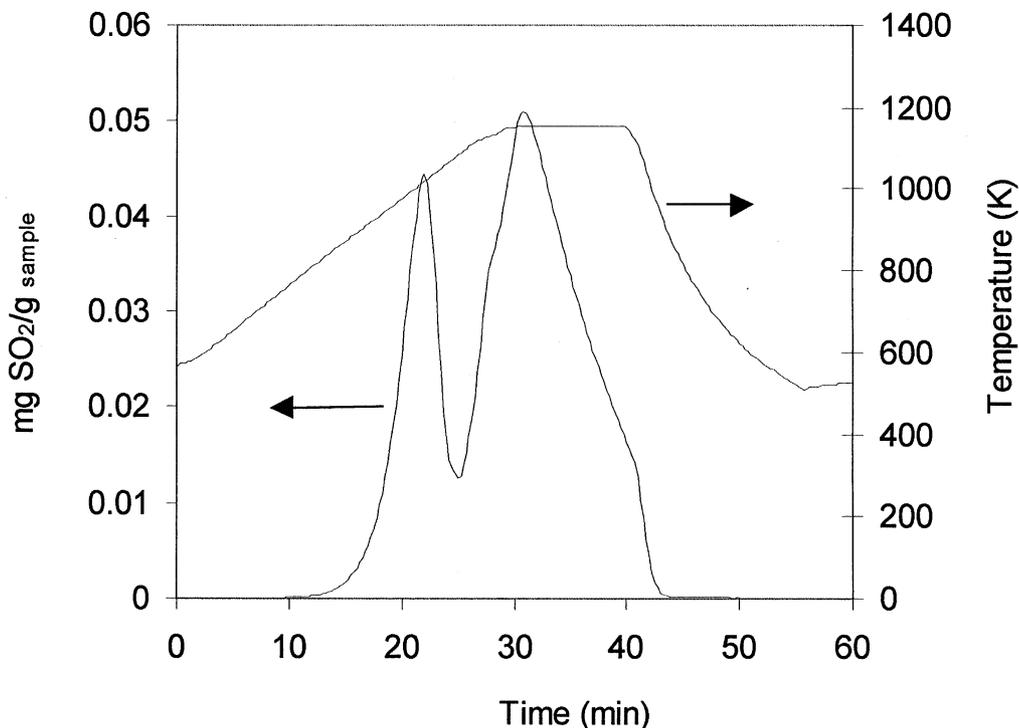


Fig. 3. TPD spectrum of the regeneration process in N₂, up to 1153 K, of CaO after SO₂ retention.

3.2.2. Study of CaSO₃ conversion into CaSO₄ to CaS

As stated above, the CaSO₃ disproportionation according to route (2) can also explain the significant decrease in SO₂ retention capacity after regeneration.

In situ XRD has been performed with the sorbent submitted to a SO₂ retention process to analyse the different species formed during the regeneration treatment in N₂. The first diffractogram has been performed at 298 K, and after

thermal treatment in N₂ at 5 K/min up to 1073 K, recording the XRD pattern every 100 K.

Fig. 4 shows the diffractograms obtained, in which the peaks have been assigned to the corresponding species. The first diffractogram, monitored at 298 K, presents peaks characteristic of Ca(OH)₂, probably formed during the handling of the sample after the SO₂ retention step. This finding is not surprising because the efficiency of calcium

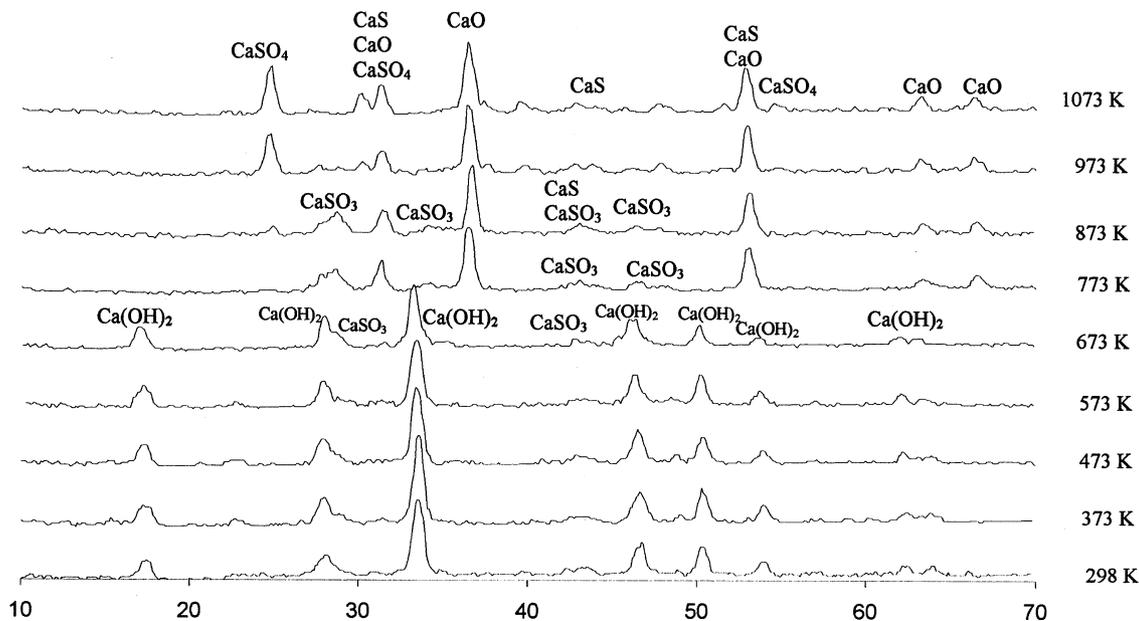


Fig. 4. In situ XRD patterns of Ca(OH)₂ sample taken during an in situ regeneration step in N₂ up to 1073 K.

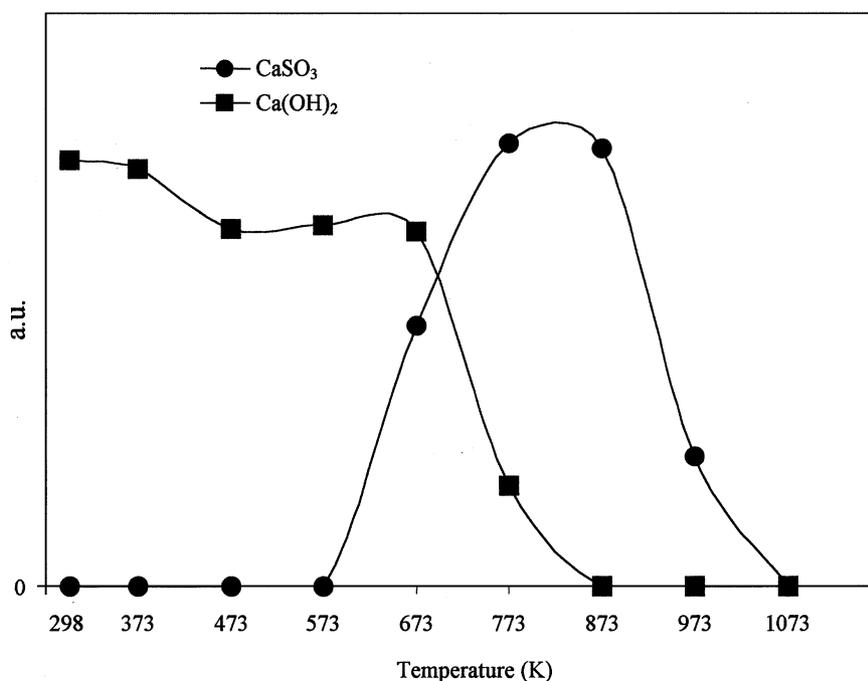


Fig. 5. Deconvoluted peak areas evolution versus heat treatment temperatures for Ca(OH)_2 and CaSO_3 areas.

oxide is only about 25%, and this species presents an important trend towards the hydration and carbonate formation when exposed to the environment [14]. As previously said, at low temperatures, the calcium carbonate is mainly formed on the surface of the calcium oxide [15,21,22] and that is why no peaks assignable to calcium carbonate are detected by XRD.

At 673 K and above, the hydroxide signals disappear, and those corresponding to calcium oxide begin to grow, corroborating the IR data. The peaks, corresponding to calcium sulphite, disappear at 973 K, according to the expected CaSO_3 decomposition [7,11,16]. Also, the presence of calcium sulphate and calcium sulphide is detected from 873 K. Therefore, the conversion reaction (2) occurs concurrently with the thermal decomposition of CaSO_3 .

Fig. 4 presents a broad peak located around a 2θ value of 29° . The deconvolution of this band shows that this signal is actually a combination of two peaks, assigned to Ca(OH)_2 at 28.6° and CaSO_3 at 29.5° . The areas of these peaks, once deconvoluted (expressed as arbitrary unities), are plotted in Fig. 5 as a function of the temperature at which every diffractogram is monitored.

The band assigned to Ca(OH)_2 is observed at low temperatures but the signal decreases significantly around 673–773 K as a consequence of the Ca(OH)_2 decomposition to CaO , which occurs around 723 K [7,14].

On the other hand, the band assigned to CaSO_3 is not observed at low temperatures confirming that only surface CaSO_3 is formed until 573 K. Only at higher temperatures (673–973 K) the signal of the CaSO_3 is observed, suggesting an increase in the CaSO_3 particle size.

In summary, Fig. 4 enables two important observations to be made: CaSO_4 and CaS have been detected as a consequence of CaSO_3 conversion above 973 K and CaSO_3 surface is transformed into CaSO_3 bulk at temperatures of 673 K and higher.

4. Conclusions

The results obtained allow us to propose a model for CaO regeneration (Fig. 6) in which Ca(OH)_2 decomposition, formation of surface CaSO_3 , change from surface to bulk CaSO_3 and CaSO_3 decomposition are considered.

- *Ca(OH)₂ decomposition:* Two factors are determined to obtain CaO with a high active surface area, desirable for the SO_2 retention process. (1) The choice of Ca(OH)_2 as the calcium precursor, that provides the best results in calcium dispersion and (2) the temperature of the thermal treatment, that must allow a complete decomposition of the precursor [18] but to avoid the increase of the CaO particle size. The scheme depicted in Fig. 6 (step 1) shows the evolution of water, due to Ca(OH)_2 decomposition and the formation of well dispersed CaO (high surface area CaO).
- *Formation of surface CaSO₃.* The number of moles of CO_2 retained at 573 K per mol of CaO , are equal to the mol number of SO_2 . This observation suggests that the formation of CaSO_3 occurs only at the surface of the CaO , as it is represented in the model (step 2).
- *Transition from surface to bulk CaSO₃:* During the

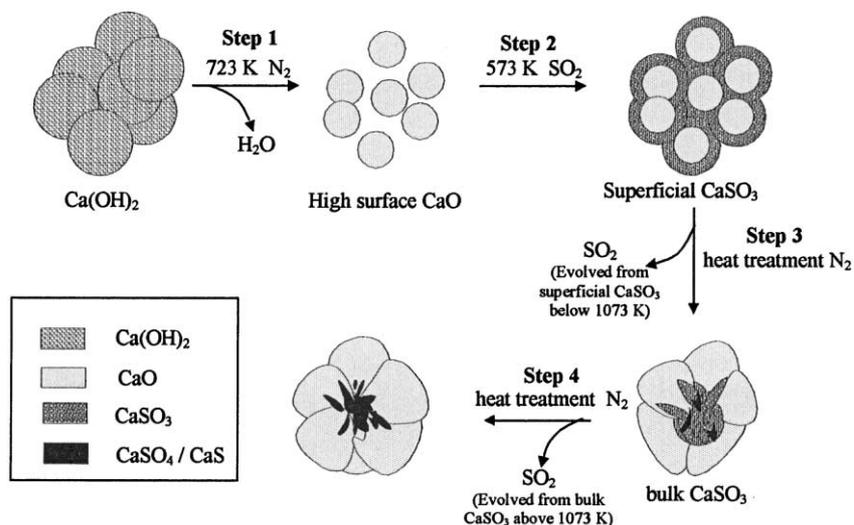


Fig. 6. Schematic proposed model to represent the reactions studied in this work.

thermal treatment at 1153 K in N_2 , after SO_2 retention at 573 K, an 88% of the CaO active surface area is lost. This decrease in surface area is promoted not only by the thermal treatment, but also by the presence of $CaSO_3$. From TPD experiments the SO_2 evolution coming from surface or from bulk $CaSO_3$ decomposition has been assessed. The results show that 72% of the $CaSO_3$ originally formed has been transformed to bulk compound by a sinterisation–agglomeration. This process, reflected in the model scheme (step 3), concurrent with the SO_2 evolution from $CaSO_3$ decomposition, leaves the remaining $CaSO_3$ trapped between CaO particles.

- *Bulk $CaSO_3$ decomposition*: The last step of Fig. 6, concurrent with the step 3, represents the decomposition and the disproportionation of the bulk $CaSO_3$.
- *Overall regeneration process*: The thermal regeneration process causes a significant loss in the sorbent capacity to retain SO_2 due to an important loss in CaO active surface. This reduction is caused by a $CaSO_3$ disproportionation (12%) and by an increase in the CaO particle size (88%).

To improve the sorbent characteristics after the regeneration process, two alternatives need further studies: (1) The use of an inert dispersing agent that minimises the CaO active area decrease and (2) the optimisation of the thermal treatment increasing the heating rate and decreasing the time at the highest temperature.

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