

# Thermogravimetric analysis of the water vapor addition during the CaO carbonation process at moderate temperatures (40–70 °C)

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**Abstract** Experiments were performed on calcium oxide, using water vapor with N<sub>2</sub> or CO<sub>2</sub> as carrier gases, between 40 and 70 °C. A initial experiment was performed with water vapor in the presence of N<sub>2</sub> to elucidate the possible hydroxylation process produced by water vapor exclusively. On the other hand, when CO<sub>2</sub> was used as carrier gas the CaO reactivity changed, producing different hydrated, hydroxylated, and carbonated phases. On the basis of these results and the fact that under dry conditions CO<sub>2</sub> is not absorbed on CaO at  $T < 70$  °C, a possible CaO–H<sub>2</sub>O–CO<sub>2</sub> reaction mechanism was proposed, where CaO superficial hydroxylation process seems to play a very important role during the CO<sub>2</sub> capture. Finally, a kinetic analysis was produced to compare the temperature and humidity relative influence on the whole process.

**Keywords** Calcium oxide · Chemisorption · CO<sub>2</sub> capture · Thermogravimetric analysis

## Introduction

Carbon dioxide (CO<sub>2</sub>) is produced in huge amounts during the fossil fuels combustion, contributing to global climate changes [1–3]. One possible solution to this threatening problem is to trap CO<sub>2</sub>. In that sense, different materials have been proposed as possible CO<sub>2</sub> captors, earth alkaline oxides among them [4, 5]. Magnesium and calcium oxides have been deeply studied as possible CO<sub>2</sub> captors, although

calcium oxide (CaO) has shown to possess much better CO<sub>2</sub> capture properties [6–16].

In addition, mineral carbonation between CO<sub>2</sub> and different natural magnesium and calcium materials is a reaction process with geological implications [17–20]. Therefore, the reaction path for the CaO–CO<sub>2</sub>–H<sub>2</sub>O system at low temperatures (from room temperature to 70 °C) is of great interest in different fields. In this sense, only few papers have studied the CO<sub>2</sub> capture in humid systems [21–25]. However, all of these analyses have been performed at relatively high temperatures ( $T > 200$  °C).

Therefore, the aim of this work was to study systematically the different physicochemical phenomena and mechanisms present during the steam hydration process of CaO in the presence of CO<sub>2</sub> at low temperatures (40–70 °C).

## Experimental

Calcium oxide (CaO) was prepared by calcining calcium carbonate (CaCO<sub>3</sub>, Sigma-Aldrich) at 900 °C for 8 h. Afterward, the CaO was characterized by X-ray diffraction (XRD), using a diffractometer D8 Advance from Bruker coupled to a copper anode X-ray tube. The presence of crystalline phases was confirmed by fitting the diffraction pattern with the corresponding Joint Committee Powder Diffraction Standards (JCPDS). After the structural analysis, CaO was texturally studied by N<sub>2</sub> adsorption–desorption. The surface area of the sample was determined by N<sub>2</sub> adsorption, using the BET model [26]. The equipment used in this case was a Minisorp II from Bel-Japan, at 77 K using a multipoint technique. Samples were previously activated at room temperature for 24 h in vacuum.

For water sorption analyses, different dynamic experiments were carried out on a temperature-controlled

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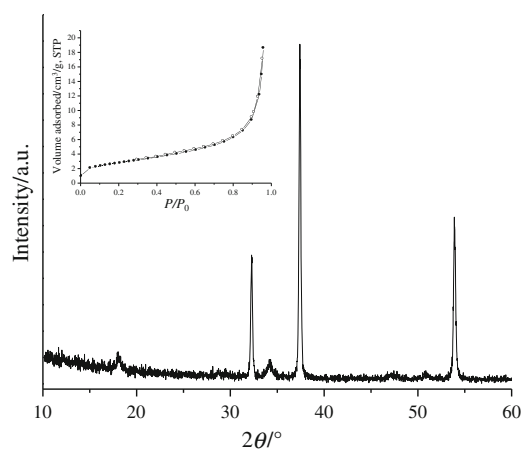
thermobalance Q5000SA from TA Instruments, equipped with a humidity-controlled chamber. The experiments were carried out using  $N_2$  or  $CO_2$ , both Praxair (grades 4.8 and 3.0, respectively), as carrier gases and distilled water as the vapor precursor, using in all the cases a total gas flow of  $100 \text{ mL min}^{-1}$ . The relative humidity (RH) percentages were controlled automatically with the Q5000SA equipment. The different water vapor sorption/desorption isotherms were generated varying temperature, between 40 and 70 °C, from 0 to 80 to 0 % of RH at  $0.5 \text{ \% min}^{-1}$ . Then, another set of samples were analyzed isothermally, fitting temperature (40 and 60 °C) and relative humidity (20, 40, 60, and 80 %). It has to be mention that some of the experiments, randomly, were repeated two or three time in order to corroborate the reproducibility.

In order to identify the products obtained after the hydration processes, the samples were characterized by standard thermogravimetric analysis (TG) and Fourier transform infrared spectroscopy (FTIR). For the TG analyses, the experiments were performed under air atmosphere, with a heating rate of  $5 \text{ °C min}^{-1}$  into a thermobalance TA Instruments model Q500HR. For the FTIR spectroscopy, analyses were performed on a Spectrometer NICOLET 6700 FTIR, using a diffuse reflectance mode.

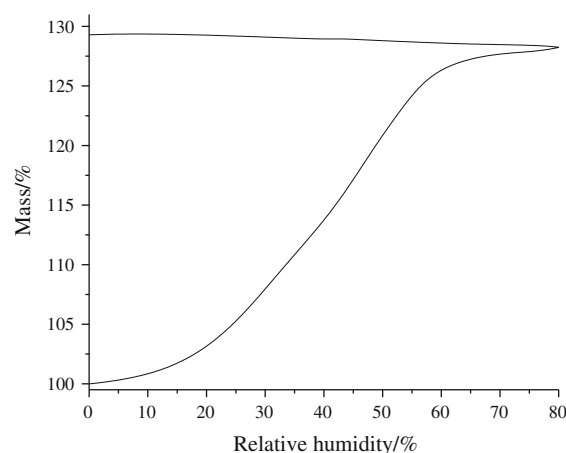
## Results and discussion

Calcium oxide was obtained from the  $CaCO_3$  calcination process at 900 °C for 8 h. Figure 1 shows the XRD pattern obtained after the thermal treatment. This pattern fitted to the 48-1467 JCPDS file, which corresponds to CaO. In addition, two small peaks were detected at  $18^\circ$  and  $34.5^\circ$  in  $2\theta$ , which correspond to superficial calcium hydroxide formed with the environmental water. After this structural characterization, the textural properties of the sample were determined by  $N_2$  adsorption–desorption (square inset of the Fig. 1). The isotherm was of type II, exhibiting a very narrow H3-type hysteresis loop, according to the IUPAC classification [26]. This behavior corresponds to nonporous dense aggregate particles. The surface area, determined using the BET model, was equal to  $9.7 \text{ m}^2 \text{ g}^{-1}$ .

An initial water vapor isotherm was performed using  $N_2$  as carrier gas at 60 °C.  $N_2$  was used, as an inert gas, to elucidate exclusively the water effect on CaO. Figure 2 shows the  $CaO-N_2-H_2O$  isotherm, which presented a curve type V, during the adsorption process, according to the IUPAC classification [26]. Furthermore, this isotherm presented an open hysteresis loop. The results show that CaO gained 29.1 % after the water sorption isotherm and during the desorption process the mass did not change significantly. This result strongly suggests that water was not only adsorbed but chemically trapped, or absorbed, on



**Fig. 1** XRD pattern of the obtained calcium oxide (CaO) synthesized by solid stated reaction. The *square inset* shows the  $N_2$  adsorption–desorption isotherm of the same sample

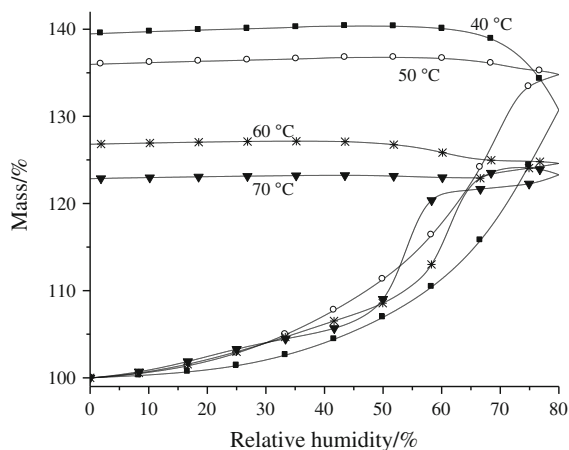


**Fig. 2** Water vapor isotherm of the CaO sample, generated at 60 °C, using  $N_2$  as carrier gas

the CaO particles. Then, part of the mass increment must be attributed to a water adsorption, while the other part may correspond to a hydroxylation process of the CaO particles, according to the following reaction:



After the analysis performed on CaO using  $N_2$ , similar experiments were performed, but now using  $CO_2$  as carrier gas, at different temperatures between 40 and 70 °C. In these cases, the curves presented isotherms type III and V, [26] as a function of the temperature (Fig. 3). At 40 °C, CaO presented an isotherm type III and the highest mass increment (39.3 %) after the desorption process. Then, experiments performed at 50 °C, and higher temperatures, presented isotherms type V and the final mass increments decreased as a function of temperature. A detailed analysis of these three curves shows that initially, between 0 and

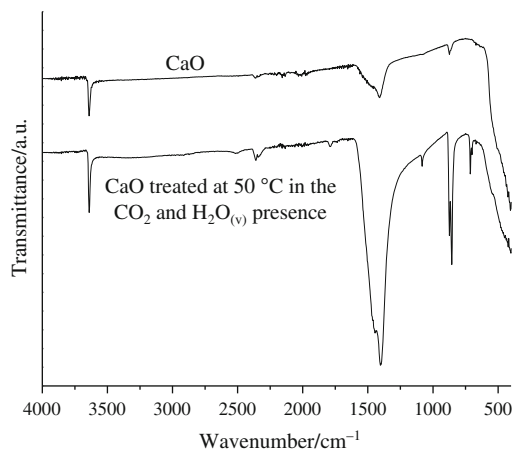


**Fig. 3** Water vapor isotherms of the CaO sample, generated at different temperatures (40, 50, 60 and 70 °C), using CO<sub>2</sub> as carrier gas

30 % of RH the mass increments ( $\sim 4$  wt %) varied as a function of temperature, but between 30 and 48 % of RH the mass increments were favored inversely to temperature. Actually, the largest mass increment was obtained on the sample treated at 50 °C (9.9 %). After that, sample treated at 70 °C increased importantly its mass between 48 and 60 % of HR, up to 22 %. Samples treated at 60 and 50 °C presented similar behaviors than that observed at 70 °C, but the mass increments were produced at higher RH (62 and 68 %, in average) and they were higher (24.6 and 34.9 %). Finally, desorption processes did not showed any significant variation on the sample's mass. The samples treated at 50, 60, and 70 °C presented final mass increments of 35.8, 26.6, and 23.0 %, respectively. From these results, it seems that there are two different processes taking place: While the carbonation process must be activated by the superficial hydroxylation, the water adsorption is reduced due to the temperature, which increases the water evaporation.

In order to probe this hypothesis and to further understand the water sorption–desorption isotherms, different FTIR and TGA experiments were performed on the samples after the water sorption–desorption processes. Figure 4 shows the FTIR spectra of the following samples; CaO original and sample previously humidity treated at 50 °C into a CO<sub>2</sub> flux.

The original sample presented the metal–oxygen vibration bands (Ca–O) between 400 and 630 cm<sup>-1</sup> [27, 28]. In addition, hydroxyl species were identified at 3,650 cm<sup>-1</sup> [27]. Then, certain degree of carbonation was evidenced due to presence of two vibration bands at 850 and 1,410 cm<sup>-1</sup>, which must correspond to CaCO<sub>3</sub>, produced over the CaO surface due to the environmental interaction. The bands at around 2,238 cm<sup>-1</sup> correspond to the environmental CO<sub>2</sub> [27, 28]. Humidity-treated sample presented similar FTIR spectra. Metal–oxygen vibration bands

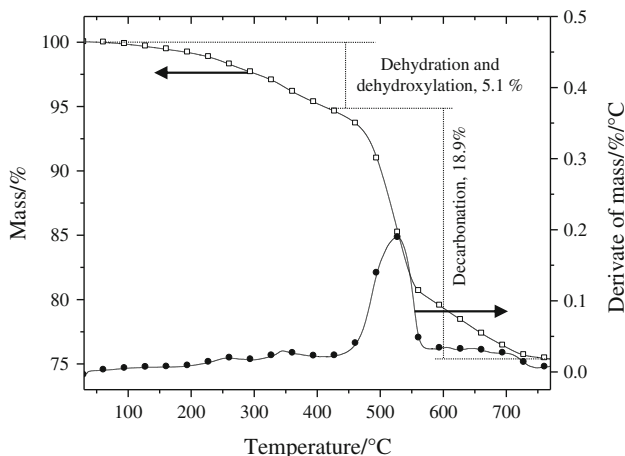


**Fig. 4** Infrared spectra of initial CaO sample and humidity-treated sample treated at 50 °C with CO<sub>2</sub>

(between 400 and 630 cm<sup>-1</sup>) were present in a similar way, where carbonate (850 and 1410) hydroxyls (3,650 cm<sup>-1</sup>) bands increased significantly. However, in this case, two additional vibration bands were detected at 1,084 and 728 cm<sup>-1</sup>. According to the literature [28], these bands may indicate the calcium bicarbonate (Ca(HCO<sub>3</sub>)<sub>2</sub>) formation. This result confirms that the mass increment observed on the humidity samples can be attributed to different carbonation processes.

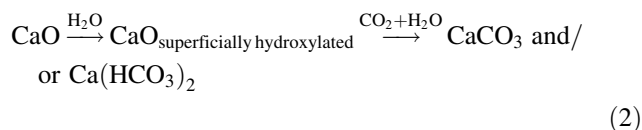
Therefore, in order to quantify the hydroxylation and carbonation degrees produced on the humidity-treated samples, some of them were analyzed by TG. Figure 5 shows the TG analysis of the sample previously treated at 70 °C into a H<sub>2</sub>O–CO<sub>2</sub> flux. From this thermogram, different mass losses can be seen. Initially, between room temperature and 430 °C, the sample lost mass corresponding to the dehydration and dehydroxylation processes of the different phases present. The mass lost corresponded to 5.1 %. This loss of mass seems to be a continuous process, which must be produced due to the water diffusion through the carbonate species which was formed on the surface of the CaO particles. Then, at temperatures higher than 450 °C, the sample presented the highest loss of mass (18.9 %), which corresponded to the decarbonation process. This result is in good agreement to the FTIR spectra and it can be established that almost 20.0 % of the mass increment is due to the carbonation process. The small differences (1.4 %) observed between this TG curve and the mass capture during the H<sub>2</sub>O–CO<sub>2</sub> process (see Fig. 3) must correspond to the CO<sub>2</sub> previously present in the CaO sample.

It is well known that CaO is not able to trap CO<sub>2</sub> at low temperature, under dry conditions, and the CO<sub>2</sub> chemisorption is only produced at  $T > 200$  °C [11–16]. Therefore, the presence of water vapor must activate the CaO particles, producing Ca(OH)<sub>2</sub> at the particle surfaces, as it



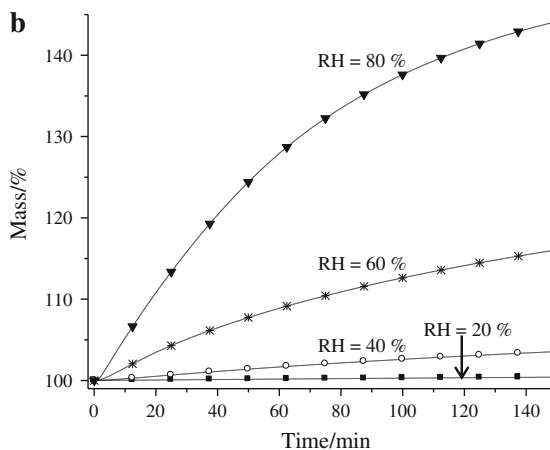
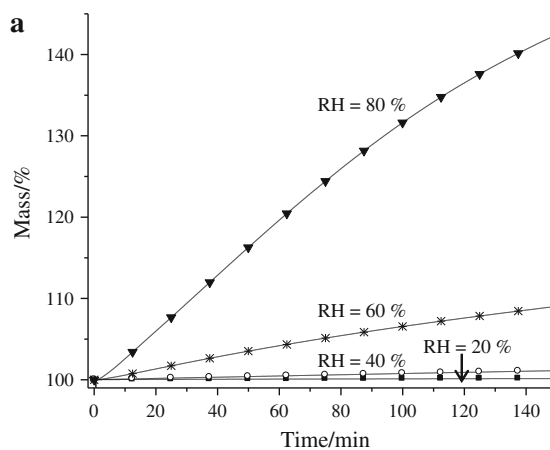
**Fig. 5** TG and DTG curves of the CaO sample previously treated with water vapor at 70 °C, using CO<sub>2</sub> as carrier gas

was shown previously. Then, the CaO-activated surface must enable the CO<sub>2</sub> capture at low temperatures (40–70 °C) producing CaCO<sub>3</sub> and/or Ca(HCO<sub>3</sub>)<sub>2</sub>. Therefore, the possible reaction mechanism must be:

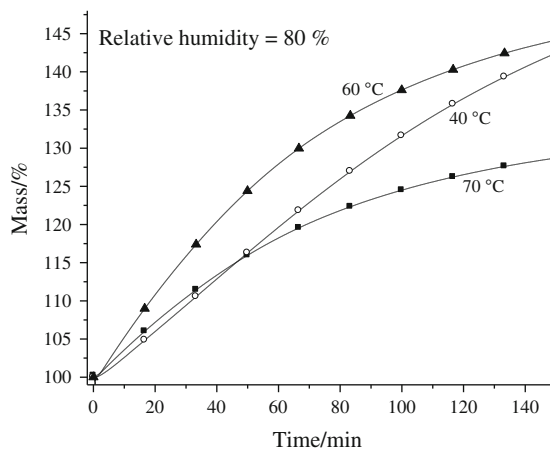


In order to further understand the CO<sub>2</sub>–H<sub>2</sub>O reactivity on CaO, different isotherms are presented on Fig. 6, which correspond to the experiments performed at different temperatures and relative humidity. All these experiments presented similar exponential behaviors, attributed to the CaO carbonation, hydration, and hydroxylation. It is clearly evident that mass increments varied as a function of relative humidity after 150 min. For example, when temperature was fixed at 40 °C, isotherms presented the following behavior. The mass increment was equal to 0.2 and 1.1 % with a relative humidity of 20 and 40 %, respectively. In both cases, the mass increment would be considered as negligible. Then, mass gained was importantly increased up to 9.0 and 42.5 % at 60 and 80 % of relative humidity, respectively (Fig. 6a). In this case, if the RH was increased, the total mass gained increased as well. A similar behavior was observed when CaO was treated at higher temperatures. As an example, Fig. 6b presents the isotherms performed at 60 °C.

Nevertheless, isothermal curves, performed at the same relative humidity, did not present a consistent trend between them when temperature was increased. Figure 7 shows the three different isothermal experiments performed at 80 % of relative humidity and different temperatures. Although isotherms presented a mass increment between 40 and 60 °C, it decreased importantly at 70 °C. In addition, at



**Fig. 6** Isotherms of H<sub>2</sub>O–CO<sub>2</sub> on the CaO sample varying relative humidity (from 20 to 80 %) at different temperatures: **a** 40 °C and **b** 60 °C



**Fig. 7** Isotherms of H<sub>2</sub>O–CO<sub>2</sub> on the CaO sample varying temperatures (from 40 to 70 °C) at a RH of 80 % (A)

short times (0–45 min), the isotherm performed at 70 °C presented a higher mass gain, in comparison to the isotherm performed at 40 °C. These results may be explained as a

function of the hydroxylation and water evaporation processes. As it was discussed above, initially a superficial hydroxylation must be produced on the CaO particles, and this chemical change must induce the subsequent carbonation process. Then, the superficial carbonates may allow some water adsorption, which decreased inversely to temperature. Nevertheless, it has to be taken into account that the  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{HCO}_3)_2$  percentages might not be the same at the different temperatures and RH values.

## Conclusions

The experiment performed using  $\text{N}_2$  as carrier gas showed that CaO is able to trap water, where the final quantity of water trapped depends on the superficial hydration, but mainly by an hydroxylation process. This result indicates that CaO is chemically altered by the presence of water in this temperature range.

If  $\text{CO}_2$  was used as a carrier gas, the CaO sample also trapped water physically and chemically, but in this case  $\text{CO}_2$  was absorbed as well, producing  $\text{CaCO}_3$  and/or  $\text{Ca}(\text{HCO}_3)_2$ . Water physically trapped decreased as a function of temperature. The isothermal analysis showed that  $\text{CO}_2$  capture is more favored by the humidity relative than temperature in this temperature range.

Finally, according to the literature, CaO is able to absorb  $\text{CO}_2$  at around  $T > 200$  °C in dry conditions. Therefore, water vapor presence improved importantly the  $\text{CO}_2$  absorption, at least on this temperature range (40–70 °C). To explain this behavior, an initial CaO superficial hydroxylation was considered as a surface activation process. However, it has to be mentioned that although water presence induce the  $\text{CO}_2$  capture in CaO at low temperatures, the reaction process may not be completed, due to different kinetic processes.

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