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Thermokinetic analysis of the MgO surface carbonation process in the presence of water vapor

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ABSTRACT

Experiments were performed on magnesium oxide, using water vapor with N_2 or CO_2 as carrier gases, between room temperature and 70 °C, in order to elucidate its thermal stability. Initial experiments were performed with water vapor in the presence of N_2 to elucidate the different physicochemical processes produced by water vapor exclusively, as N_2 is an inert gas. These results showed that water is only adsorbed on the MgO surface. On the other hand, when CO_2 was used as carrier gas the MgO reactivity changed, producing hydrated magnesium carbonate, due to the CO_2 absorption. On the basis of these results and the fact that under dry conditions CO_2 is not absorbed on MgO at $T < 70\,^{\circ}C$, a possible MgO–H_2O–CO_2 reaction mechanism is proposed, where MgO microstructural parameters play a significant role during the CO_2 absorption.

1. Introduction

Since the beginning of the industrial revolution, the use of fuels has become an essential part of the human life. Therefore, carbon dioxide (CO_2) concentrations have been increased dramatically, producing climate changes through the green house effect [1–3]. In that intelligence, several propositions have been published in the last years for the CO_2 absorption or adsorption, concentration and its possible elimination [1,4–6]. Among these propositions, magnesium oxide (MgO), as well as other alkaline earth metal oxides, has been used in different manners [7–9]. For instance, MgO has been studied as a possible CO_2 absorbent mainly because of its low energy requirement for regeneration (compared to other oxides), although it possesses a low absorption capacity due to kinetic factors [6,9]. Furthermore, in the last years MgO has been proposed as a catalytic support of different processes. For example, the synthesis of combined steam and carbon dioxide reforming of methane (CSCRM) [10–17].

Additionally, mineral carbonation between CO_2 and different natural magnesium and calcium silicates (olivine, serpentine and wollastonite among others) is a reaction process with geological implications [1,18,19]. Therefore, the reaction path for the MgO–CO_2–H_2O system at low temperatures (from room temperature to 70 °C) is of great interest in different fields. In this sense, most of the studies performed up to now have been developed in aqueous systems where magnesium oxide, or magnesium ceramics, is dispersed [18,20]. For example, Xiong and Lord [19] reported the CO_2 capture on a MgO aqueous suspension, where $Mg(OH)_2$ is initially produced and then $Mg(OH)_2$ reacts with CO_2 producing different hydrated magnesium carbonates. However, the MgO hydration and carbonation processes, where H_2O is present as vapor, and not in solution, has not been studied. This kind of systems would be of high interest, for example, on different catalytic systems or during the CO_2 absorption processes, where the water and CO_2 quantities may be controlled in order to improve the corresponding processes.

Therefore, the aim of this work was to study systematically the different physicochemical phenomena and mechanisms present during the steam hydration process of MgO in the presence and absence of CO_2.

2. Experimental

Magnesium oxide was obtained by the magnesium carbonate ($MgCO_3$, Aldrich) thermal decomposition at 800 °C for 8 h. The composition, structure and microstructural properties of MgO were confirmed by X-ray diffraction (XRD) and N_2 adsorption (data not shown). For XRD a diffractometer Bruker AXS D8 Advance was used coupled to a copper anode X-ray tube. MgO was identified conventionally by its corresponding Joint Committee Powder Diffraction Standard (JCPDS) file. Textural properties of MgO were determined by N_2 adsorption. The equipment used in this case was

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a Minisorp II from Bel-Japan at 77 K using a multipoint technique. Sample was previously activated at 200 °C for 24 h in vacuum. N_2 adsorption–desorption isotherm indicates the presence of certain mesoporosity and the BET surface area was 29.5 m^2/g.

For water vapor analyses, different dynamic experiments were carried out on a temperature-controlled thermobalance Q5000SA from TA Instruments, equipped with a humidity controlled chamber. The experimental variables were temperature and relative humidity (RH). Experiments were carried out using N_2 or CO_2, both Praxair (grades 4.8 and 4.0, respectively), as carrier gases and distilled water as the vapor precursor, using in all the cases a total gas flow of 100 mL/min. First, different water vapor isotherms were generated varying temperature, between 40 and 70 °C, from 0 to 80% and then from 80 to 0% of RH. After those experiments, and in order to identify the hydration products, hydrated powders were characterized by standard thermogravimetric (TG) and infrared (FTIR) analyses. For the TG analysis, experiments were performed under air atmosphere with a heating rate of 5 °C/min by a thermobalance TA Instruments model Q500HR. For the FTIR spectroscopy samples were analyzed by a Spectrometer NICOLET 6700FT-IR.

3. Results and discussion

Water vapor isotherms were performed using N_2 as carrier gas. N_2 was used, as an inert gas, to elucidate exclusively the effect of water on the MgO particles between room temperature and 70 °C. Fig. 1 shows the MgO–H_2O isotherms at different temperatures. Water isotherms presented curves type III, during the adsorption process, according to the IUPAC classification [21]. Furthermore, these isotherms presented hysteresis loops, and most of them did not close. A detailed analysis shows that MgO gained different water quantities as a function of temperature. Sample treated at 40 °C presented the highest increment of weight, 5.9 wt.%. Then, final weights decreased as a function of temperature. While samples thermally treated at 50 and 60 °C increased their weight in only 2.8 and 2.2 wt.%, sample treated at 70 °C practically did not retained water at the end of the experiment. These results strongly suggest that water was only adsorbed on the MgO surface particles, and weights gained would be attributed to superficial hydration processes of the MgO particles. Additionally, water adsorption decreased as a function of temperature due to a higher evaporation rate promoted by the temperature increments. In a previous work, Xiong and Lord [19] reported the MgO hydroxylation at room temperature. However, in that case, MgO was doped with different elements and those experiments were performed for much longer times (up to 1245 days), in aqueous solutions. Therefore, in that case the hydroxylation process must be controlled by kinetic factors and the presence of doping elements.

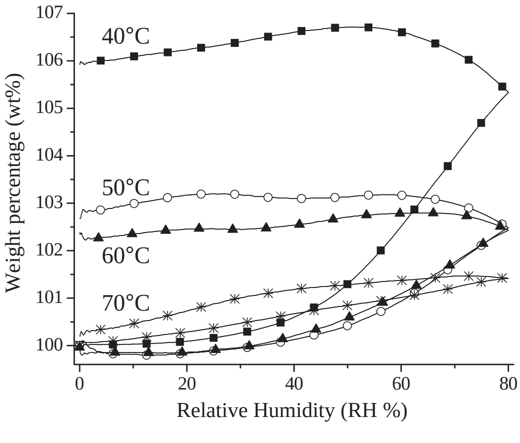

Fig. 1. Water vapor isotherms of the MgO sample, generated at different temperatures (40, 50, 60 and 70 °C), using N_2 as carrier gas.

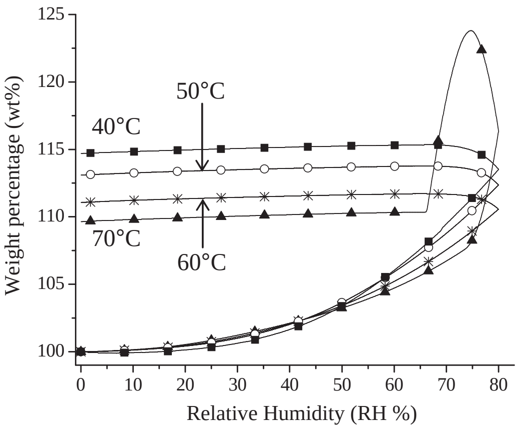

Fig. 2. Water vapor isotherms of the MgO sample, generated at different temperatures (40, 50, 60 and 70 °C), using CO_2 as carrier gas.

After the analysis performed on MgO using N_2, similar experiments were performed, but now using CO_2 as carrier gas. Again, as in the N_2 case, curves presented type III isotherms, according to the IUPAC [21] (Fig. 2). However, weight variations, using CO_2, were larger than those observed previously using N_2, and the weights gained decreased as a function of temperature. From these results, it may be assumed that MgO surface reactivity was increased with the CO_2 addition, perhaps producing a mixture of $MgCO_3$ and adsorbed water (it was corroborated below). Something else has

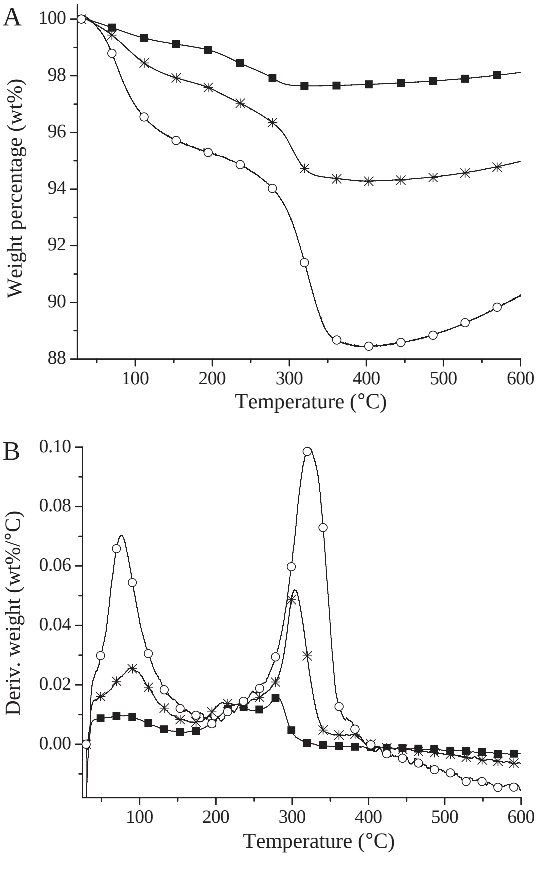

Fig. 3. TG (A) and DTG (B) curves of the initial MgO sample (■); and MgO humidity-treated at 60 °C with N_2 (*) or CO_2 (○), as carrier gases.

to be pointed out; although MgO is thermodynamically able to absorb CO_2 at room temperature [9], experimentally MgO absorbs CO_2 at $T \geq 300\,^{\circ}C$ due to kinetic factors [22]. Therefore, water vapor seems to improve the CO_2 absorption at lower temperatures. Additionally, at 70 °C the isotherm presented an atypical behavior. In this temperature isotherm increased its weight very importantly when RH reached values between 60 and 80%. It can be explained as a higher water adsorption produced on the $MgCO_3$, previously formed.

To corroborate the carbonation reaction during the thermal-hydration process, different TG and FTIR analyses were performed. Fig. 3 shows the TG and DTG results obtained for the MgO initial sample as well as the MgO samples humidity treated at 60 °C with N_2 and CO_2 as carrier gases. It is evident that although the three samples presented similar trends, the thermal-humidity conditions in which each sample was tested during the H_2O isothermal experiments modified the corresponding weight loss. Initially, MgO sample practically did not lose weight between room temperature and 100 °C, while MgO humidity-treated samples lost between 2 and 4 wt.%, as it would be expected, and which is merely water adsorbed. Then, when temperature was increased to 200 °C, samples presented two different losses of weight consecutively, as it can be seen in the DTG curves. The weight loss produced at around 224 °C was attributed to a small dehydroxylation process. However, the main process was produced between 280 and 324 °C, depending on the sample, which corresponds to a decarbonation process. Part of the carbonates were present since the beginning of the experiments, as it can be seen in the original sample, and the rest of them should be absorbed during or after the hydration process, in the samples treated with CO_2 and N_2, respectively. From the derivate curves (Fig. 3B), it can be seen that decarbonation average temperatures are slightly shifted to higher temperatures when CO_2 was used as carrier gas, which may be attributed to kinetic factors as a consequence of the higher carbonation presented by this sample. Something else has to be pointed out from these thermograms; water desorption increased as follows: MgO < MgO humidity treated with N_2 < MgO humidity treated with CO_2. Therefore, it seems that water adsorption is improved, probably due to the MgO surface carbonation (see description of the reaction mechanism below).

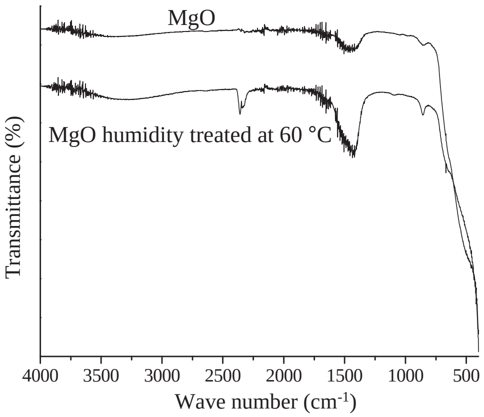

Fig. 4. Infrared spectra of initial MgO sample and humidity-treated sample treated at 60 °C with CO_2.

Fig. 4 shows the FTIR spectra of the following samples; MgO and MgO humidity-treated at 60 °C with CO_2. MgO sample presented two important band vibrations; the first one centered at 1448 cm^{-1}

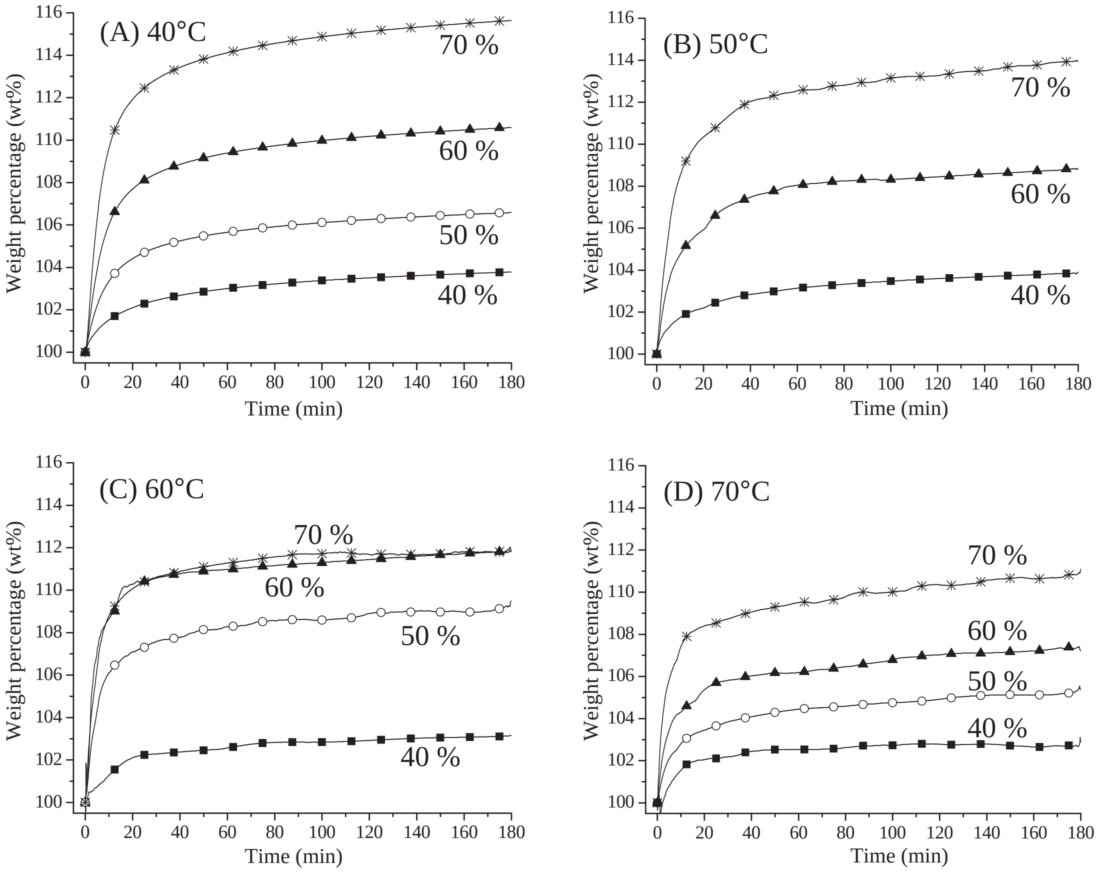

Fig. 5. Isotherms of H_2O–CO_2 on the MgO sample varying relative humidity (from 40 to 70%) at different temperatures (40, 50, 60 and 70 °C).

and the second one at lower values than 500 cm^{-1}. The vibration band located between 500 and 400 cm^{-1} corresponds to the Mg–O vibrations [23]. On the contrary, the vibration band centered at 1448 cm^{-1} corresponds to $-CO_3$ vibrations [23,24]. Therefore, MgO sample contains a certain degree of $MgCO_3$, which may be produced from an environmental spontaneous carbonation. Then, MgO sample humidity treated at 60 °C presented a similar FTIR spectrum. However, in this case the vibration band centered at 1448 cm^{-1} ($-CO_3$ vibrations) was importantly increased, which indicates a higher carbonation. A second vibration band was elucidated in this sample at 860 cm^{-1}, which can be associated to carbonates [24]. Additionally, this sample presented a very narrow vibration band between 3500 and 3000 cm^{-1}, which should correspond to O–H vibrations of some water molecules adsorbed [23,24]. These FTIR results confirm that MgO is able to absorb CO_2 in the presence of water vapor, as it was previously seen by TG analysis.

In order to further understand the CO_2–H_2O reactivity on MgO, different isotherms are presented on Fig. 5, which correspond to the experiments performed at different temperatures and RHs. All these experiments presented similar exponential behaviors, attributed to the MgO carbonation and hydration. However, weight increments varied as a function of temperature and RH. For example, when temperature was fixed at 40 °C, isotherms presented the following behavior. The weight increment was equal to 3.7 wt.% with a RH of 40%. Then, weight gained was importantly increased up to 6.6, 10.5 and 15.8 wt % at 50, 60 and 70% of RH, respectively (Fig. 5A). In this case, if the RH was increased, the total weight gained increased as well. A similar behavior was observed when MgO was treated at 50, 60 and 70 °C. However, total weight increments decreased when temperature was increased. As it was discussed above, it must correspond to a higher evaporation rate induced by temperature increments.

A different, but interesting behavior is observed, when isotherms are compared as a function of the RH (Fig. 6). Again, the final weight gained decreased as a function of temperature. This result corroborates the fact that water evaporation rate is increased due to temperature. Nevertheless, the isothermal behavior was different during the first moments (3 min). Here, temperature improved weight increments. Therefore, to explain this behavior it would be established that carbonation process is produced during the first moments and this reaction is thermally favored. Then water adsorption must be produced over the $MgCO_3$ surface material.

Based on all these results it would be possible to propose a reaction mechanism. In the literature, it has been proved that water vapor modifies, positively, the CO_2 absorption on different alkaline and alkaline earth ceramics [4,25–28]. For example, Essaki et al. found that humidity increases CO_2 absorption on lithium orthosilicate Li_4SiO_4 at room temperature [26]. Authors proposed that carbonate layer formed on the ceramic surface during absorption might be dissolved in water thus, in this way, absorption is promoted. On the other hand, Siauciunas and coworkers [27] studied the Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) carbonation. As in the previous case, authors suggested an intermediate hydrolysis reaction but additionally they consider the formation of more reactive species into the Tobermorite structure as a result of its microstructural properties (surface area and porosity). Then, as MgO does not seem to absorb CO_2 in dry conditions in this temperature range, the formation of intermediate species must be promoted by the MgO microstructure, perhaps by the mesoporosity presented in the sample, in which water vapor condensed, dissolving CO_2. This CO_2 dissolution must enhance the MgO–CO_2 reactivity. $MgCO_3$ is produced as a consequence of this enhanced reactivity, which induces a higher water adsorption, as it was seen on the experiments performed at 70 °C (see Fig. 2). Therefore, water vapor has a double effect on the MgO–CO_2 reaction system: initially, water vapor promotes the formation of $MgCO_3$, and secondly water vapor is adsorbed on the $MgCO_3$ product.

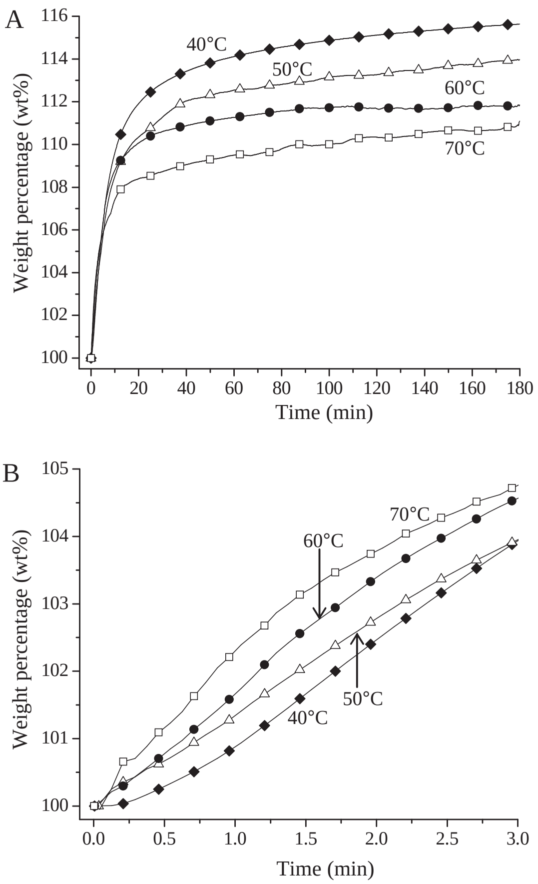

Fig. 6. Isotherms of H_2O–CO_2 on the MgO sample varying temperatures (from 40 to 70 °C) at a RH of 70% (A). The second panel (B) shows the first 3 min of the same isotherms.

4. Conclusions

Experiments performed using N_2 as carrier gas clearly showed that MgO is able to adsorb water, where the final quantity of water adsorbed depends on temperature, as it could be expected. These results indicate that MgO stability is not chemically altered by the presence of water, in this temperature range. Later, when CO_2 was used as carrier gas, MgO sample continued adsorbing water, but in this case by a different mechanism. Here, CO_2 was absorbed producing magnesium carbonate at the MgO surface particles; water was then subsequently adsorbed in higher quantities, as magnesium carbonate is a much higher hygroscopic material. The total weight gained under these conditions was twice higher than that observed using N_2. This weight increment was produced by the $MgCO_3$ appearance and consequently the higher hydration. Finally, according to the literature, MgO is able to absorb CO_2 at around 300–400 °C in dry conditions. Therefore, water vapor presence improved the CO_2 absorption, at least on this temperature range (40–70 °C). To explain this behavior, different microstructural factors were taken into account.

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