

Analysis of the CO₂ capture in sodium zirconate (Na₂ZrO₃). Effect of the water vapor addition

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ABSTRACT

Sodium metazirconate (Na₂ZrO₃) was synthesized, by solid-state reaction, and characterized. Water sorption experiments were performed using N₂ and CO₂ as carrier gases. In the absence of CO₂, Na₂ZrO₃ showed considerably high water vapor sorption owing to two different processes, hydroxylation and water vapor adsorption. When CO₂ was used as the water vapor carrier gas, the reactivity of Na₂ZrO₃ was found increased as a result of the reaction producing NaHCO₃ and ZrO₂. These results reveal that, at least in the measured temperature range, Na₂ZrO₃ is able to take-up 2 mol of CO₂ compared to 1 mol of CO₂ measured under dry conditions, as the final product is sodium bicarbonate (NaHCO₃). In other words, the theoretical CO₂ absorption capacity on Na₂ZrO₃ is 10.8 mmol/g, when water vapor is added. Finally, a kinetic analysis and the reaction mechanism are presented for Na₂ZrO₃ carbonation process in the water vapor presence.

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1. Introduction

Since the beginning of the industrial revolution, the use of fuels has become an essential part of the human life. Additionally, in the same period of time, the population on the earth has grown continuously in a considerably way. As a consequence of these two factors, among others, the pollution produced in our planet has increased dramatically, where one of the most important pollution types corresponds to the air pollution. In that way, most of the air pollution is produced from the combustion of fossil fuels. The combustion of these materials (coal, oil and gas among others) has raised the carbon dioxide (CO₂) amounts in the atmosphere to levels never seen before (Schrag, 2007). Therefore, in order to solve this threatening problem, several proposals have been established; where a possible key means, for reducing the green house effect, is to capture, separate and concentrate CO₂ (Busch et al., 2008; Leuning et al., 2008; Figueroa et al., 2008; Oexmann et al., 2008).

In that sense, different alkaline ceramics have been considered as possible CO₂ captors (Olivares-Marín et al., 2010; Ida et al., 2004; Yi and Eriksen, 2006; Fauth et al., 2005; Tsumura et al., 2005; Zhao et al., 2010; Ávalos-Rendón et al., 2009; Palacios-Romero and Pfeiffer, 2008; Rodríguez-Mosqueda and Pfeiffer, 2010; Togashi et al., 2007; Nair et al., 2009), where several of these

works mention that CO₂ absorption is modified by water vapor (Nair et al., 2009; Martínez-dlCruz and Pfeiffer, 2010; Essaki et al., 2004; Ochoa-Fernández et al., 2009). However, this phenomenon has not been fully characterized. Among these materials, sodium zirconate (Na₂ZrO₃) is considered as a possible CO₂ captor (Ochoa-Fernández et al., 2009; López-Ortiz et al., 2004; Alcérreca-Corte et al., 2008; Zhao et al., 2008). Nevertheless, there are not so many papers showing water vapor effects during the CO₂ absorption on this ceramic. Chen and coworkers (Ochoa-Fernández et al., 2009) showed that water vapor has an important impact in the CO₂ absorption and regeneration kinetics, as well as in the stability of lithium and sodium zirconates. Later, Martínez-dlCruz and Pfeiffer (2010) described the water sorption mechanism on K-doped Li₂ZrO₃ in presence and absence of CO₂.

On the other hand, despite different research efforts water sorption process, on different surfaces, is not totally understood (Henderson, 2002; Lange et al., 2009; Ranke and Xing, 1997). However, water–solid surface interactions are very important for different physical and chemical processes (Henderson, 2002; Li et al., 2009; Salman and Katiroglu, 1998; Cicero et al., 2004; Dulub et al., 2005; Meng et al., 2007). Additionally, alkaline ceramics tend to be hygroscopic materials (Cotton and Wilkinson, 1999). Therefore, the presence or absence of water vary importantly their superficial and even bulk characteristics, which may consequently modify their possible applications.

Therefore, the aim of the present work was to study, systematically, the physicochemical phenomena that take place during the Na₂ZrO₃ hydration processes, in presence and absence of CO₂.

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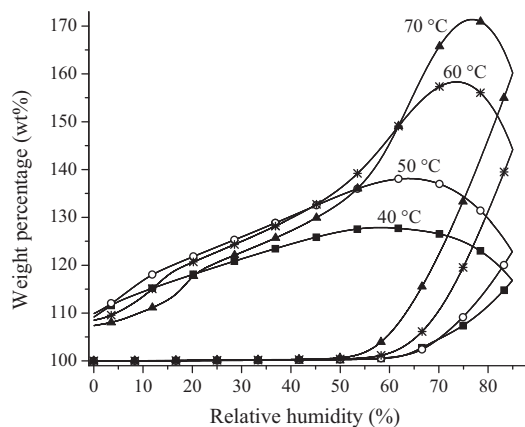


Fig. 1. Na_2ZrO_3 water sorption/desorption isotherms at different temperatures, using N_2 as carrier gas.

Then, different kinetic analyses are presented, and a water sorption mechanism is proposed.

2. Experimental

Synthesis and characterization. Sodium zirconate (Na_2ZrO_3) was synthesized by solid-state reaction. The reagents were zirconium oxide (ZrO_2 ; Aldrich) and sodium carbonate (Na_2CO_3 ; Aldrich), where the Na_2CO_3 : ZrO_2 molar ratio was 1.1:1.0. Reagents were mechanically mixed and then fired at 850°C for 6 h. The ceramic composition was confirmed by XRD (data not shown). Additionally, sample surface area was determined by N_2 adsorption, using the BET model (Rouquerol et al., 1999). Na_2ZrO_3 presented a surface area of $1.7\text{ m}^2/\text{g}$.

Water sorption analyses. Dynamic and isothermal experiments were carried out on a humidity-controlled thermobalance (TA Instruments, model Q5000SA) at different temperatures and relative humidity (RH). The experiments were performed using distilled water and two different gases: nitrogen (N_2 , Praxair grade 4.8) and carbon dioxide (CO_2 , Praxair grade 3.0). The total flow gas used in all the experiments was $100\text{ mL}/\text{min}$ and the RH percentages were controlled automatically by the Q5000SA equipment. Dynamic water vapor sorption/desorption experiments were generated at different temperatures (between 30 and 70°C), varying the RH from 0 to 85% and then from 85 to 0% at the following rate: $0.5\%/ \text{min}$. Additionally, different isothermal experiments were performed at specific temperatures and RH for 180 min, using N_2 and CO_2 as carrier gases. Afterwards, sample products ($\sim 3\text{ mg}$) were characterized in order to identify the hydration products. As the product masses were very small, some samples were analyzed by thermogravimetric analysis (TGA) and the others by infrared (FTIR) spectroscopy. For TG analyses, experiments were performed under air atmosphere with a heating rate equal to $5^\circ\text{C}/\text{min}$ into a thermobalance TA Instruments, model Q500HR. For FTIR spectroscopy, samples were analyzed in a Spectrometer NICOLET 6700 FTIR.

3. Results and discussion

Fig. 1 shows the Na_2ZrO_3 water sorption–desorption curves, using N_2 as carrier gas. Sorption isotherms corresponded to type III, according to the IUPAC classification (Rouquerol et al., 1999), which indicates that the attractive adsorbate–adsorbent interactions are relatively weak and that the adsorbate–adsorbate interactions play an important role. Water sorption varied as a function of temperature, and water sorption was not completed or limited to sorption curves. Even, during some part of the desorption process,

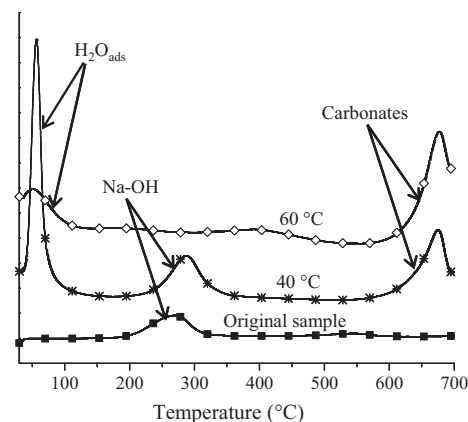
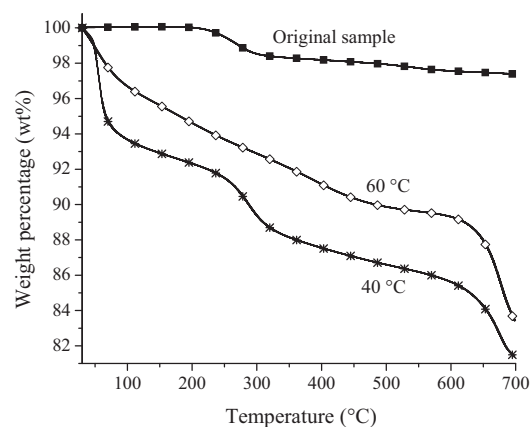


Fig. 2. TG and DTG curves of the original and heat-humidity treated Na_2ZrO_3 samples, under a N_2 flux.

samples gained weight. When Na_2ZrO_3 sample was treated at 40°C , water sorbed was equal to 27.3 wt%, but this quantity increased as a function of temperature up to 71.5 wt% at 70°C . During desorption process, curves presented two different slopes: The first desorption was produced at high RH and it may be attributed to water evaporation produced over the Na_2ZrO_3 surface. On the other hand, the second process (at RH equal or lower than 22%) should correspond to water evaporation of water molecules occluded into inter-particle sites, for instance triple points. All Na_2ZrO_3 samples gained different weights at the end of these experiments, which varied inversely to temperature, perhaps due to a higher evaporation process. Final weight gained may be attributed to H_2O physical and/or chemically sorbed.

Therefore, in order to analyze the Na_2ZrO_3 hydration products some of those samples were analyzed by TGA. Fig. 2, shows the TG and DTG analyses of the original and Na_2ZrO_3 samples thermal-humidity treated. Thermal curve, of the original sample, shows a unique lost of 1.5 wt%, between 210 and 315°C . It corresponds to a dehydroxylation process of Na-OH superficial species (Boxiong et al., 2006). When Na_2ZrO_3 sample was previously humidity-treated at 40°C , its thermogram changed. Initially, this sample lost 6 wt% before 100°C , which corresponded to water evaporation. Then, a dehydroxylation process was evidenced between 250 and 320°C as in the original sample. The weight lost corresponding to the dehydration and dehydroxylation processes fit well with the final weight increment observed during the dynamic sorption–desorption curves $\sim 10\text{ wt}\%$ (see Fig. 1). Finally, a third weight lost was produced at temperatures higher than 610°C , which corresponded to superficial decarbonation process. Carbonates were not present on the original sample, so CO_2 must be absorbed, from the environment, after water sorption–desorption

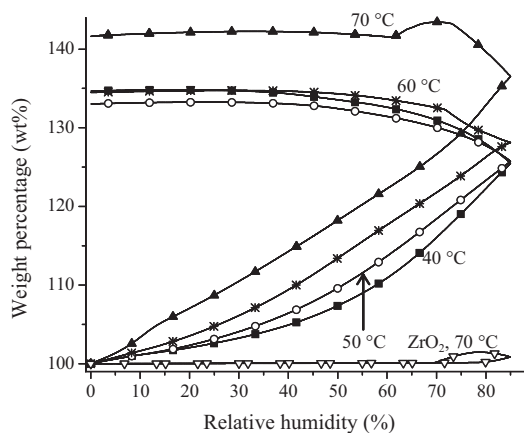


Fig. 3. Na_2ZrO_3 water sorption/desorption isotherms at different temperatures, using CO_2 as carrier gas.

experiments. Perhaps, superficial hydroxyls may have induced sample carbonation. Furthermore, it should be pointed out that these carbonates must be present on the Na_2ZrO_3 surface as bulk Na_2CO_3 decomposes at temperatures higher than 800°C . Sample humidity-treated at 60°C presented a similar behavior than that observed on the previous sample. However, in this case water adsorbed and hydroxyl formations decreased in 2–3 wt%, in comparison to the sample treated at 40°C . This result confirms that temperature on the sorption–desorption experiments increased the water evaporation, and subsequently the hydroxylation must be reduced as well, but not eliminated, as superficial carbonates were still found.

After the water sorption analysis with N_2 , similar experiments were performed but now using CO_2 as carrier gas. Fig. 3 presents the Na_2ZrO_3 isotherms performed with CO_2 . Additionally, in this figure is presented a similar isotherm performed on ZrO_2 for comparison purposes. This sample presented a similar qualitative behavior than that observed on the Na_2ZrO_3 sample treated with N_2 , isotherms type III (Rouquerol et al., 1999). Nevertheless, the weight increments began practically since the beginning of the experiment using CO_2 , and the final weight increments were three times higher than those observed using N_2 (see Fig. 1).

If CO_2 is being chemically trapped, Na_2ZrO_3 may decompose producing ZrO_2 . Then, to elucidate whether or not ZrO_2 is producing part of the CO_2 –water vapor sorption, it was equally tested. ZrO_2 isotherm at 70°C is presented in Fig. 3, and as it can be seen ZrO_2 practically did not show any increment of weight, which clearly indicates that ZrO_2 does not absorb H_2O and/or CO_2 .

Na_2ZrO_3 hydrated samples (samples obtained as products of the experiments performed in Fig. 3) were characterized by TGA and FTIR. Fig. 4 shows the TG and DTG curves of the samples humidity-treated at 40 and 60°C . During the thermal experiments, at 100°C , both samples presented an important weight lost. Na_2ZrO_3 sample treated at 60°C lost almost two times more weight (17 wt%) than the sample treated at 40°C (9 wt%). This thermogram shape does not correspond to an evaporation process (Hatakeyama and Zhenhai, 1998). Therefore, a decomposition process may have occurred. Later, between 250 and 370°C samples lost between 2 and 3 wt%, which can be attributed to superficial dehydroxylations. Finally, at temperatures higher than 550°C samples began to loss weight, which must correspond to decarbonation. It has to be mentioned that both samples had gained 35 wt%, approximately, after the thermal-humidity treatments (see Fig. 3). However, in these thermograms samples did not loss the same weight percentage, they only loss 25 and 28 wt%. In fact, the main difference was observed at 100°C , where the Na_2ZrO_3 sample treated at 60°C lost

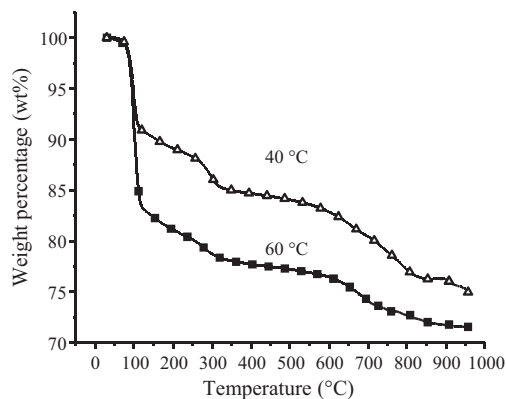


Fig. 4. TG curves of two different heat-humidity treated Na_2ZrO_3 samples after the CO_2 capture process.

almost two times more weight than the sample treated at 40°C . This result suggests that, different species may be produced as a function of the temperature and some of them have not been eliminated in the thermograms, due to bulk diffusion processes.

Fig. 5 shows the FTIR spectra of the following Na_2ZrO_3 samples; original and samples previously humidity-treated at 50 and 70°C , as well as humidity-treated at 50°C with a second thermal treatment at 150°C . The original sample presented the metal–oxygen vibration bands (Na–O and Zr–O) between 400 and 750 cm^{-1} (Ali and Kaki, 1998; Nakamoto, 2009; Miller and Wilkins, 1952). Additionally, hydroxyl species were identified between 3000 and 3500 cm^{-1} (Nakamoto, 2009). Then, certain degree of carbonation was evidenced due to presence of two vibration bands at 850 and 1410 cm^{-1} , which correspond to Na_2CO_3 . On the contrary, humidity treated samples presented a totally different FTIR spectra. Although metal–oxygen vibration bands (between 400 and 750 cm^{-1}) were present, carbonate (850 and 1410 cm^{-1}) and O–H (3000 – 3500 cm^{-1}) bands tended to disappear. However, new vibration bands appeared at 698 , 840 , 1000 , 1035 , 1050 , 1295 , 1460 , 1630 , 1660 , 1906 and 2500 cm^{-1} . Actually, all these vibration bands fitted with the NaHCO_3 FTIR spectrum (Hatakeyama and Zhenhai, 1998). This result explains the weight loss produced at 100°C on TG analyses, which must correspond to NaHCO_3 decomposition to Na_2CO_3 . In order to confirm the NaHCO_3 decomposition to Na_2CO_3 , the Na_2ZrO_3 sample previously humidity-treated at 50°C was heat treated at 150°C and air cooled down immediately. This

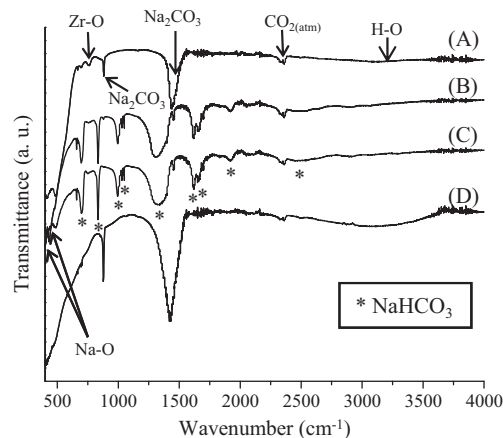


Fig. 5. FTIR spectra of the original and heat-humidity treated Na_2ZrO_3 samples: (A) Na_2ZrO_3 original sample, (B) Na_2ZrO_3 sample treat at 50°C in presence of H_2O and CO_2 , (C) Na_2ZrO_3 sample treat at 70°C in presence of H_2O and CO_2 and (D) Na_2ZrO_3 sample treat at 50°C in presence of H_2O and CO_2 after a second thermal treatment at 150°C under air. The NaHCO_3 vibration bands were labeled as (*).

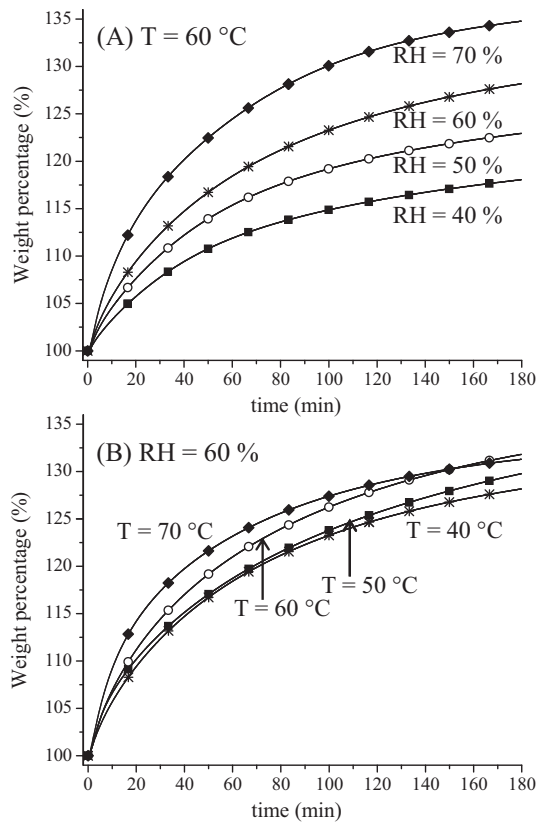
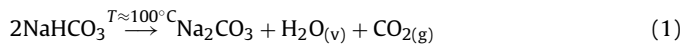


Fig. 6. Kinetic isotherms performed at different temperatures (40, 50, 60 and 70 °C) and relative humidity (40, 50, 60 and 70%) using CO₂ as carrier gas.

temperature was chosen according to the TGA results (see Fig. 4). The FTIR of this sample (Fig. 5D) clearly shows that NaHCO₃ disappeared, and the Na₂CO₃ vibration bands are evidenced at around 850 and 1400 cm⁻¹. Therefore, the initial weight lost observed on the thermograms (Fig. 4) corresponds to the following NaHCO₃ decomposition process:



This reaction system shows that CO₂ captured on Na₂ZrO₃, in the H₂O_(v) presence, can be partially desorbed at low temperatures.

To understand the CO₂–H₂O reactivity on Na₂ZrO₃, different kinetic experiments are presented in Figs. 6 and 7, which correspond to the experiments performed at different temperatures and

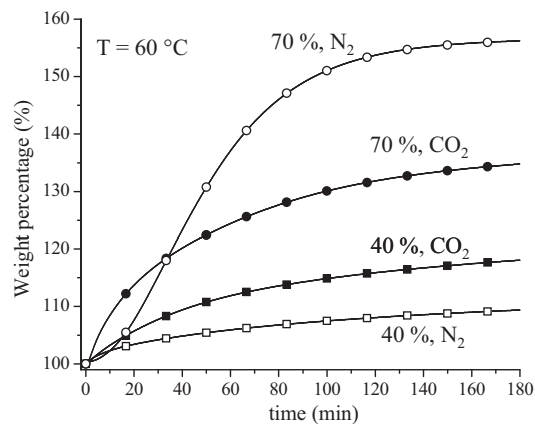


Fig. 7. Kinetic isotherms performed at 60 °C, varying the relative humidity (40 and 70%) and the carrier gas (CO₂ and N₂).

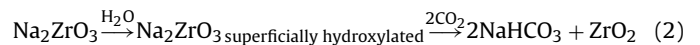
relative humidity, varying the carrier gas between CO₂ and N₂. Fig. 6A shows the isotherms performed at 60 °C varying the relative humidity and using CO₂ as carrier gas. As it can be seen, isotherms increased weight as a function of the relative humidity. While the sample analyzed with 40% of RH gained 17.6 wt% after 180 min, the sample treated with 70% of RH gained 34.3 wt% in the same period of time. On the other hand, when samples are compared as a function of temperature, they did not showed significant variations. For example, when samples were analyzed with 60% of RH the weight increments were only of around 27.7 and 32.5 wt%, varying temperature from 40 to 70 °C. As it can be seen, CO₂–H₂O sorption process is more affected by RH than by temperature.

Finally, a different and interesting behavior is observed if the isotherms are compared as a function of the carrier gas. Fig. 7 shows several isotherms performed at 60 °C varying the RH (40 and 70%) and the carrier gas (CO₂ and N₂). It can be seen that at 40% of RH the sample treated with CO₂ gained more weight (18.3 wt%), than the sample treated with N₂ (9.8 wt%). On the other hand, at high RH (70%) samples behaved inversely at long times; while the sample treated with CO₂ only gained 35.1 wt% after 180 min, the sample treated with N₂ increased its weight up to 55.7 wt% in the same period of time. The differences observed on the weight increments among these two experiments must be correlated to the hydration affinity of the different compounds produced over the Na₂ZrO₃ surface particles. While sample treated with N₂ produced some hydroxyls over the Na₂ZrO₃ surface particles, sample treated with CO₂ produced mainly NaHCO₃. Then the multilayer water adsorption process must be favored on the hydroxylated surface than over the NaHCO₃ surface. In fact, these results are in good agreement with the dynamic experiments shown in Figs. 1 and 3. In those cases, the sorption processes of the samples treated with N₂ presented higher weight increments than those observed on the samples treated with CO₂, although the final weight increment were higher in the second set of samples.

It has to be mentioned that these two samples gained weight in very different ways during the first moments. At the beginning of the experiments sample treated with CO₂ gained much more weight than sample treated with N₂. Therefore, it seems that carbonation process is faster when the surface is hydroxylated.

Summarizing, water vapor modifies importantly CO₂ absorption properties on Na₂ZrO₃ at low temperatures, based on the fact that this ceramic is not able to absorb CO₂ on dry conditions in this temperature range (Pfeiffer et al., 2007). However, Na₂ZrO₃ presented a different CO₂–H₂O absorption mechanism. Initially, Na₂ZrO₃ seems to react with water vapor producing hydroxyl species at the particle surfaces, as in the previous case, which must induce the carbonation process. The hydroxylation process did not seem to be a bulk process in any case, as in both cases (N₂ and CO₂) the samples only lost 4–5 wt% due to dehydroxylations.

CO₂ absorption did not produce sodium carbonate on the water vapor presence, but sodium bicarbonate was produced (reaction (2)). Therefore, under these thermal-humidity conditions 1 mol of Na₂ZrO₃ can absorb theoretically up to 2 mol of CO₂ and 1 mol of H₂O, where the maximum weight gain should be 57.2 wt%, according to the following reaction (2):



In the present case, the maximum weight increment was equal to 35 wt%, and it was produced at 60 °C and 70% of RH. Fig. 8 shows the TG of the sample isothermally treated at 60 °C and 70% of RH. This thermogram presented the same thermal behavior than those described previously in Fig. 4, where the H₂O and half of the CO₂ is desorbed by the NaHCO₃ decomposition process (see reaction (1)). If all the Na₂ZrO₃ had reacted to produce NaHCO₃, the initial weight

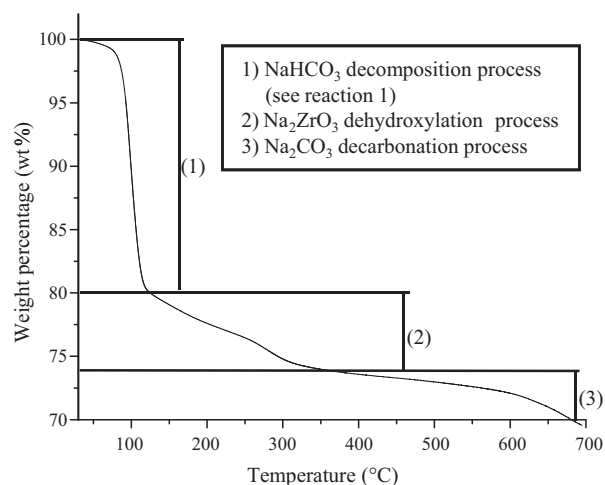


Fig. 8. TG curve of the sample previously isothermally treated at 60 °C and 70% of RH.

lost must correspond to 36.9 wt%. Therefore, an initial weight lost of 20 wt% must correspond to a CO₂ capture efficiency of 54.2%.

Na₂ZrO₃ presents much better CO₂ absorption efficiencies at high temperatures, mainly attributed to the sodium diffusion process, which is activated at $T > 400$ °C (Alcérreca-Corte et al., 2008; Pfeiffer et al., 2007). In this work, as the experiments were produced at low temperatures, sodium diffusion is not activated. Then, CO₂ absorption on Na₂ZrO₃ must be mainly associated to the water vapor presence over the surface particles.

Therefore, at low temperatures (30–70 °C) and in the presence of H₂O vapor, Na₂ZrO₃ can absorb, theoretically, up to 10.8 mmol/g of CO₂ per gram of ceramic, which is a considerable quantity, among alkaline ceramics and even other materials (Choi et al., 2009; Ávalos-Rendón et al., 2009). In the present work, Na₂ZrO₃ was able to absorb 5.8 mmol/g of CO₂. Therefore, Na₂ZrO₃ would be used as CO₂ captor not only at high temperatures, as it has been previously reported, but at relatively low temperatures as well in the presence of water vapor. In fact, the CO₂ capture in here is higher than those values reported by other materials in the same temperature range (≤ 6 mmol/g of material, Choi et al., 2009).

4. Conclusions

CO₂ sorption process of sodium zirconate (Na₂ZrO₃) was evaluated, in the presence of water vapor at low temperatures (30–70 °C). Initial results, performed using N₂ as carrier gas, showed that Na₂ZrO₃ is able to trap water by two different mechanisms; physically (adsorption) and chemically (absorption) by a surface hydroxylation. Of course, water vapor adsorption and/or absorption depended on temperature and relative humidity.

When CO₂ was used, Na₂ZrO₃ trapped water by the same mechanisms. Nevertheless, under these conditions, CO₂ was chemically trapped as well, because of the reaction producing NaHCO₃ and ZrO₂. In fact the NaHCO₃ synthesis seemed to be increased as a function of temperature, according to the TGA and FTIR analyses. It means that under the thermal-humidity conditions, Na₂ZrO₃ is able to absorb up to 10.8 mmol/g of CO₂, which is two times more CO₂ than the quantity absorbed under dry conditions. Moreover, it has to be mentioned that reactivity varied as a function of temperature and RH, and ZrO₂ does not contribute to any of the different sorption processes. Finally, it has to be said that, sodium zirconate presents better CO₂ absorption efficiencies in presence of water vapor, owing to the initial hydroxylation of the ceramic surface and thus promoting a higher CO₂ reactivity of the newly activated surfaces.

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