

A study on the ball-milling effect of calcined Mg-Al hydrotalcite on the CO₂ adsorption behavior

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We have investigated the effect of ball-milling over calcined Mg-Al hydrotalcite, with regard to its CO₂ adsorption capacity. The prepared materials were systematically characterized by X-ray diffraction, scanning electron microscopy and N₂ physisorption measurements. The results reveal an excellent adsorption capacity of CO₂ by calcined Mg-Al hydrotalcite; however, when this adsorbent was treated by ball-milling for 2 h, a slight decrease in its CO₂ adsorption capacity was observed, mainly attributable to the decreased surface area, total pore volume, pore size and the formation of particle aggregates of the aforementioned hydrotalcite. Therefore, alterations in structure, texture and morphology of calcined Mg-Al hydrotalcite during the ball-milling treatment do not optimize its CO₂ adsorption capacity.

Key words: CO₂ adsorption, Calcined Mg-Al hydrotalcite, Co-precipitation synthesis, Ball-milling effect.

Introduction

It is well-known that global warming is one of the main environmental concerns around worldwide, and that CO₂ is one of the greenhouse gases that most notably contribute to this problem [1]. Currently, it is an environmental issue of great importance that requires an immediate solution to diminish the negative impacts of high CO₂ atmospheric concentrations to the environment and ecosystems [2]. In this framework, the global scientific community has made great efforts to develop new and advanced CO₂-capture technologies as technologically viable solutions for the reduction of atmospheric CO₂ on a large scale. In this scenario, recently, one of the most promising post-combustion CO₂ capture technologies has been developed, which carries out CO₂ capture with solid adsorbents, made possible by its high operating flexibility and low energy demand; thus, from this point of view, the design of CO₂ solid adsorbents is quite viable [3, 4]. Many solid adsorbents have been actively researched and reported in specialized literature for CO₂ capture purposes [5-10]. Each one of these studied materials has shown interesting results in terms of CO₂ adsorption capacity, under different temperature and pressure conditions, but it is still necessary to find an adsorbent that exhibits high selectivity and adsorption towards CO₂; besides, great effort has been made to improve CO₂ capture. In this regard, the key requirement for

technological CO₂ capture applications is the development of new adsorbents that have a high CO₂ working retention capacity over a wide temperature range, from room temperature to 700 °C [11]. Currently, and according to literature, hydrotalcites-type adsorbents, with divalent and trivalent cations such as Mg²⁺ and Al³⁺, have demonstrated exceptional CO₂ capture due to their unique characteristics, such as anion-exchange, high surface area and a considerable layer-charge, significant with regard to acidic gases, as in the case of CO₂ [12-14]. Hydrotalcites can be obtained commercially, as well as in a laboratory; they are double-layered hydroxides with lamellar structure, formed by a positively-charged brucite layer, with an interlayer space to accommodate water molecules and CO₃²⁻ anions. Also, these materials have presented high stability during cycling operations, which is crucial for the development of practical applications such as CO₂ capture [15, 16]. It has been reported in the literature, that the maximum CO₂ capture capacity of hydrotalcite compounds are generally found in the temperature range of 200-400 °C [17-19]. On the other hand, it has also been confirmed that the adsorbent surface area plays an important active role in CO₂ adsorption, because it translates to a greater number of active sites which, in turn, represent greater adsorbance. To address this issue, different strategies have been examined in recent years in order to improve adsorbent activity [20-23]. In particular, the strategies that include reducing the adsorbent particle-size to nanometric scale (<100 nm) have proved to be promising methodologies for improving adsorbent activity, because the generated fine nanoparticles have higher contact and reaction efficiencies than traditional materials do [24]. It is well-

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known that the ball-milling mechanical activation method provides an efficient route for preparing stabilized nano-size adsorbents with improved structural, chemical and textural characteristics that could be relevant for CO₂ capture [25]. The mechanical ball-milling method is an extensive method employed to obtain nanostructured materials with several technological uses [26-27]; this mechanical ball-milling treatment allows to activate dry solids and specifically increase their surface area, as well as to improve their CO₂ capture properties [28]. Thus, it is considered to have a broader impact compared to other conventional materials. With regards to hydrotalcite-like compounds, the recent interest in novel mechanochemical approaches is devoted almost exclusively to the successful preparation and modification of these layered double hydroxides using different starting materials, as well as preparing different nanocomposites [29-32]. From the hydrotalcite synthesis viewpoint, the mechanochemical activation method is simple and versatile, reduces time consuming, and avoids heating treatment, solvent use and production of large amounts of waste, which are characteristics consequences of other existing synthesis methods such as urea hydrolysis, sol-gel, hydrothermal, combustion, sonication, microwave irradiation, steam activation and solvothermal [33]. So far, however, significantly fewer studies have indicated that the ball-milling process, as a nanoparticle generation method, enhances CO₂ capture [11, 25].

With regard to this concern, studies need to be conducted in order to determine the effect of ball milling over the CO₂ adsorption behavior of hydrotalcites in order to optimize this process. To the best of our knowledge, no study has been reported on CO₂ adsorption behavior of calcined Mg-Al hydrotalcite after ball-milling. Therefore, new results could contribute to a greater understanding of the CO₂ adsorption mechanism. For these reasons, the aim of this study was to understand the effectiveness of the calcined Mg-Al hydrotalcite, followed by ball-milling treatment for CO₂ capture, as a viable CO₂ capture process, because of the expected formation of aluminum and manganese oxide coatings over the Mg-Al calcined hydrotalcite surface, which may provide different adsorption sites and a higher surface area for enhanced CO₂ adsorption due to its resultant nanostructured nature.

Experimental Procedure

The Mg-Al hydrotalcite used in this study was synthesized by the co-precipitation method at constant pH, according to Sato *et al.* [34]. This procedure is based on the mixing of solutions *A* and *B*; solution *A* contains the cation precursors of hydrotalcite (Mg²⁺ and Al³⁺) in water and solution *B* consists of NaOH

and NaCO₃ compounds, which provides a basic medium of pH between 8-10, sufficient for hydrotalcite formation and precipitation. These carbonates participate in the stabilization of hydrotalcite structure as load compensators, due to its large size, which facilitates the filtration of the precipitate formed. Then, using a classic procedure, 1,000 mL of a solution of MgCl₂·6H₂O 0.75 M and AlCl₃·6H₂O 0.25 M were added, drop by drop, to 1000 mL of another solution, which consisted of 0.5 M Na₂CO₃ and 2.5 M NaOH, under vigorous agitation. Both aqueous solutions were previously heated to 60 °C and kept at this temperature during vigorous agitation. Once the hydrotalcite was obtained, it was separated by filtration and then washed with enough distilled water until that the chloride ions were not detectable by precipitation with silver nitrate in solution. The Mg-Al hydrotalcite precipitate was dried at room temperature for 5 days, and then dried at 80 °C in a stove for three hours. The molar ratio value of prepared hydrotalcite by this method was 0.25. Then, the calcined Mg-Al hydrotalcite, denoted as CHT, was obtained by heating the previously-prepared Mg-Al hydrotalcite to 500 °C for 5 hours in a muffle furnace; the obtained powders were cooled to room temperature and grounded to a fine powder in an agate mortar. Additionally, the CHT prepared via co-precipitation, followed by calcination, was ball-milled for 2 hours under an argon atmosphere by using a Spex 8000 high-energy mechanical mill with a 50 mL-capacity and a ball-to-powder weight ratio of 6:1. This obtained material (CHT-BM), together with the dry Mg-Al calcined hydrotalcite (CHT), were employed for CO₂ adsorption determinations.

CO₂ adsorption experiments were carried out at 200 °C and 1 atmosphere of pressure using a Parr 4592 stainless-steel pressure reactor with a 50 mL-capacity, coupled to a temperature-controlled system. Separately, 8 mg of Mg-Al hydrotalcite samples were exposed to a high-purity (99.98%), ultra-dry CO₂ gas flow for 15 minutes, as a fixed saturation time. Before the CO₂ adsorption tests, the samples were pretreated at 325 °C under vacuum for 30 min in order to remove the adsorbed environmental impurities. CO₂ adsorption capacities were determined by thermogravimetric analysis using a TGA calorimeter analyzer (TA Instruments SDT Q600), coupled to a mass spectrum analyzer (TA Instruments, LLC). In this analysis, approximately 6 mg of Mg-Al hydrotalcite samples were placed in a ceramic cell and heated from 20 °C to 850 °C at a heating rate of 10 °C/min, under an inert atmosphere, in which helium was used as the carrier gas (100 mL/min). The ratio $m/e = 44$ was used for CO₂ quantification. The number of millimoles of CO₂ captured per gram of Mg-Al hydrotalcite (mmol/g) were calculated from the TGA calcination profiles, based on the weight loss of CO₂ that was adsorbed in the materials.

Results and Discussion

XRD analysis

Fig. 1 shows the XRD patterns of the Mg-Al hydrotalcite powders prepared by the co-precipitation method after calcination at 500 °C for 5 h (CHT), and the calcined Mg-Al hydrotalcite powders after the ball-milling treatment for 2 hours (CHT-BM). Granados and Serrano [35] reported that the hydrotalcite prepared by co-precipitation before calcination showed a typical hydrotalcite pattern of sharp and intense reflections at 11.7°, 23.2°, 60.6° and 61.8°, at low values of 2θ angle, and less intense, asymmetric reflections at higher angular values, characteristic of a well-crystallized Mg-Al hydrotalcite compound, in agreement with the JCPDS card No. 41-1428, of a double-layered material composed of a positively-charged brucite-like layer and a negatively-charged interlayer, with the interlayer space typically occupied by water molecules and anions for charge compensation. The X-ray pattern of the Mg-Al hydrotalcite calcined at 500 °C for 5 h (CHT) showed that its characteristic lamellar structure disappeared, and that at this collapsed layer structure, only a well-dispersed mixture of Mg and Al oxides was obtained with a high BET-specific surface area, large total pore volume and a mesoporous diameter, as was revealed by N₂ physisorption measurements (Table 1). It is well-known that, under calcination at 400-500 °C, the Mg-Al hydrotalcite gradually loses interlamellar water up to at approximately 200 °C; in the range of 200-500 °C, it is dehydroxylated and decarbonated, allowing the formation of a well-dispersed mixture of aluminum and magnesium oxides, with a typical mixed oxide XRD trace obtained, where there are no peaks present related to aluminium oxide, because aluminum oxide does not crystallize at the relatively low temperature at which calcination is carried out.

Therefore, the X-ray diffraction pattern (Fig. 1) confirms the formation of mixed oxides through calcination. When the calcined Mg-Al hydrotalcite was ball-milled for 2 h, (labeled as the CHT-BM sample), the presence of only a mixture of Mg and Al oxides was observed in this X-ray pattern (Fig. 1), but with an increased crystallinity compared to calcined hydrotalcite. The increased crystalline structure can be attributed to the effect exerted on the adsorbent powders by the ball-milling medium (stainless-steel balls), generating a

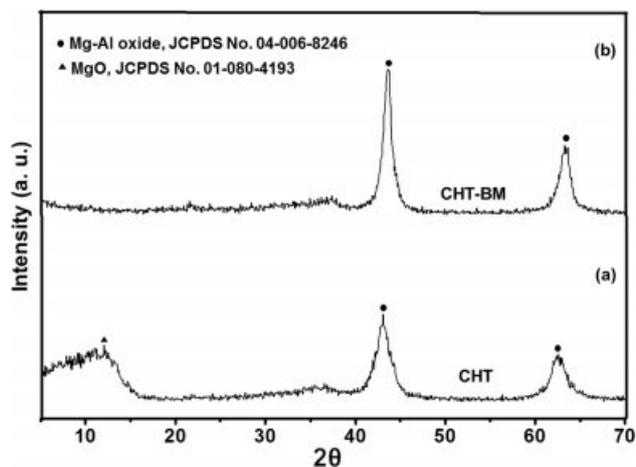


Fig. 1. XRD diffraction patterns of Mg-Al hydrotalcite samples prepared by the co-precipitation method; (a) no treatment (CHT) and (b) treatment with ball-milling for 2 h (CHT-BM).

nanostructured material with a reduced particle size, which could improve the CO₂ capture [36]. It has been previously reported that smaller metal oxide particle sizes provide a larger BET-specific surface area for exposure and, as a result, these materials have a higher CO₂ adsorption capacity. Specifically, results have shown that both MgO and CaO-based adsorbents prepared through solution-combustion synthesis and treated by ball-milling, produced metal oxide particles with better textural and structural properties for enhancing CO₂ adsorption capacity, proving that the mechanical process plays a crucial role in CO₂ adsorption behavior [20]. Thus, from this stand-point, the nanostructured nature of the CHT-BM sample should lead to greater reactivity and increased adsorption effects, involving a large number of active surface sites available for CO₂ molecules.

Morphology and EDS analysis

According to Rossi *et al.* [15], the formed mixture of alkali Mg and Al oxides after hydrotalcite calcination, are strongly related to the basic sites for the adsorption of acidified CO₂ molecules. Yang and Kim [18] reported that the basicity of hydrotalcite also depends on chemical composition (cation type, M²⁺/M³⁺ ratio, anion type existing in the interlayer) and activation conditions such as the degree of impregnation with alkali metal carbonates. In consequence, the aluminum content directly affected the hydrotalcite's CO₂ adsorption capacity,

Table 1. Main textural properties of calcined Mg-Al hydrotalcite (CHT), and calcined Mg-Al hydrotalcite after ball-milling treatment for 2 h (CHT-BM). The samples were previously degassed with N₂ at 300 °C for 2 h.

Samples	BET-specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mean pore diameter (nm)	N ₂ adsorption/desorption isotherms	Pore size distribution (BJH)*		
					r _p (nm)	A _p (m ² /g)	V _p (cm ³ /g)
CHT	191.97	0.7732	16.111	Type IV	10.76	167.07	0.7513
CHT-BM	87.25	0.1455	6.6700	Type IV	1.21	31.91	0.1204

*Barrette-Joyner-Halenda (BJH) method

because the increase in adsorbent Al content decreased the number of basic sites [15]. Therefore, based on the obtained M^{2+}/M^{3+} ratio, determined by energy-dispersive X-ray spectroscopy (EDS) analysis (Fig. 2), it is clear that the calcined Mg-Al hydrotalcite, followed by ball-milling for 2 hours, exhibited the best features, and it was to be expected that this material present the maximum CO_2 adsorption capacity. Furthermore, in this study, it was also observed (by SEM images) that the CHT-BM sample (Fig. 2) resulted in particle agglomeration after mechanical ball-milling, and that important alterations of the original morphology and textural properties, along with a predominant formation of particle agglomerates after using the ball-milling treatment, had an inverse effect on CO_2 adsorption capacity.

N_2 adsorption-desorption isotherm analysis

On the other hand, the N_2 adsorption-desorption isotherm results (Fig. 3), presented type IV isotherms of the studied samples, specifically for the CHT sample, exhibited a marked low-adsorption hysteresis between the adsorption and desorption curve, which, according to the International Union of Pure and Applied Chemistry (IUPAC), is characteristic of mesoporous materials. It is well-known that different adsorbent physicochemical characteristics such as BET-specific surface area, particle size, pore size, and pore volume, are essential characteristics that play an important role in CO_2 adsorption behavior, influencing the accessibility of CO_2 in the pore structure or adsorbent surface [36]; for example, adsorbents with a higher porosity have a greater amount of pores, which determine a significant portion of the CO_2 adsorption process, as well as

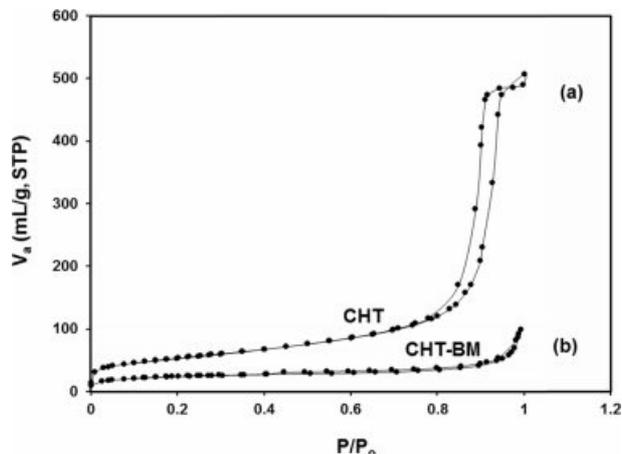


Fig. 3. N_2 adsorption-desorption isotherms of Mg-Al hydrotalcite samples prepared by the co-precipitation method; (a) no treatment (CHT), and (b) treated with ball milling for 2 h (CHT-BM).

physiadsorbents with small pores, which have shown great potential as CO_2 adsorbents. Indeed, CO_2 adsorption increases as total pore volume increases, because a large pore volume has more active sites for CO_2 , and experiences less diffusion resistance. According to the main textural results (Table 1), it can be seen that the Mg-Al hydrotalcite, followed by ball-milling for 2 h (CHT-BM) does not have the most significant physicochemical characteristics, when compared to the calcined Mg-Al hydrotalcite sample (CHT) without mechanical ball-milling treatment.

Pore size distribution analysis

In addition, a significant reduction in pore size, from

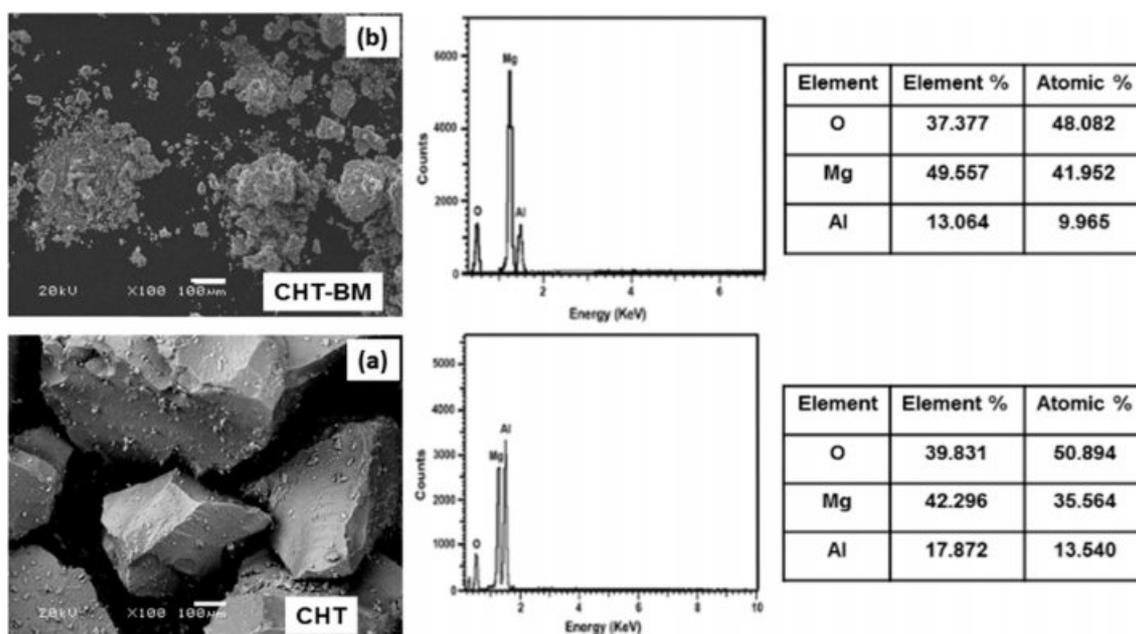


Fig. 2. SEM micrographs at 100X and EDS analysis of Mg-Al hydrotalcite samples prepared by the co-precipitation method; (a) no treatment (CHT) and (b) treated with ball-milling for 2 h (CHT-BM).

10.76 nm to 1.21 nm, obtained by the Barrett-Joiner-Halenda (BJH) pore size distribution method was also observed when the Mg-Al hydrotalcite was ball-milled (Fig. 4); this sample showed a marked decrease in pore area (A_p) and total pore volume (V_p) values (Table 1). It is known that the kinetic CO₂ molecule diameter is 0.33 nm [37] and that the Mg-Al calcined hydrotalcite, after ball-milling treatment, was drastically reduced in its pore diameter, hence, the available pore space for CO₂ did not lead to a better diffusion of CO₂ in the pore channels and decreased CO₂ adsorption.

CO₂ adsorption behavior

The CO₂ adsorption behavior of CHT and CHT-BM samples was examined. The obtained adsorption capacity values, determined by thermogravimetric analysis and differential scanning calorimetry, were different in both studied Mg-Al hydrotalcites. The TGA/DSC curves for CO₂ desorbed from the studied hydrotalcite samples are shown in Fig. 5. It can be observed that the CO₂ adsorption capacity for CHT-BM was 2.018 mmol/g, which was 5.08% less than that observed value for CHT (2.126 mmol/g). These obtained results are not consistent with those expected. The results indicate that the ball-milling treatment negatively affects CO₂ adsorption ability in the CHT-BM sample. It was expected that the surface area would increase with mechanical ball-milling; however, it was revealed that an important change occurred on the outer surface or inside the CHT-BM sample. It is reasonable to expect that a mixed oxide derived from calcined hydrotalcite, with considerable BET-surface area and high basicity, would

display an improved CO₂ adsorption, and even more reasonable to expect that the calcined Mg-Al hydrotalcite, treated by ball milling (CHT-BM), would increase in its CO₂ adsorption capacity due to its nanometric scale and nature. Based on the above, the prepared CHT-BM sample showed a decrease in its BET-surface area of 87.25 m²/g, in comparison to the calcined Mg-Al hydrotalcite (191.97 m²/g), as well as a decrease in its total pore volume, pore radius, as can be seen in Table 1.

It can be clearly observed that the original small holes and channels were blocked in the ball-milled calcined Mg-Al hydrotalcite structure (CHT-BM). This alteration lead to a decrease in BET-surface area and total pore volume, decreasing the effective reactive sites and reducing the ability of the CHT-BM sample for CO₂ capture. Also, it has been widely reported that an appropriate pore size allows the diffusion of CO₂ molecules inside of the adsorbent material; therefore, pore size can inhibit or allow diffusion of CO₂ molecules through the hydrotalcite core, and certain pore sizes are ideal for CO₂ adsorption. Consequently, an extended reduction in pore size can make the solid adsorbent unsuitable for CO₂ capture. In this regards, an average particle-size reduction, resulting in the creation of fractures after ball-milling, reduced the diffusion of CO₂ molecules into the inner framework of the CHT-BM and, as a consequence, the CO₂ capacity of CHT-BM

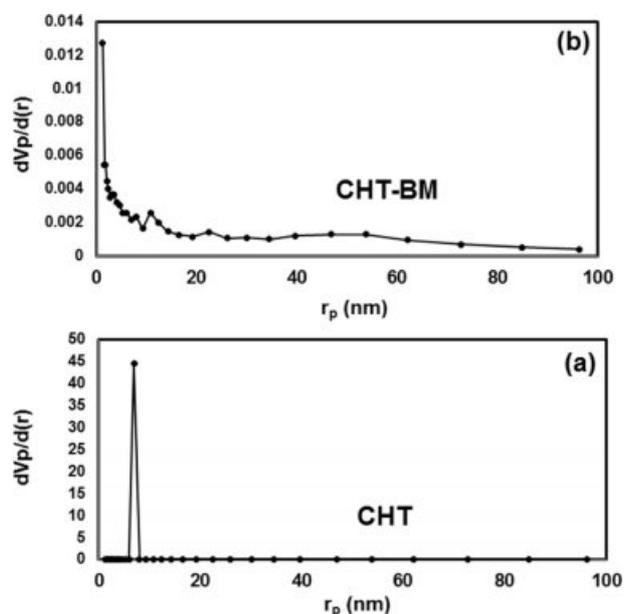


Fig. 4. Pore-size distributions by BJH method of Mg-Al hydrotalcite samples prepared by the co-precipitation method, with (a) no treatment (CHT) and (b) after treatment with ball-milling for 2 h (CHT-BM).

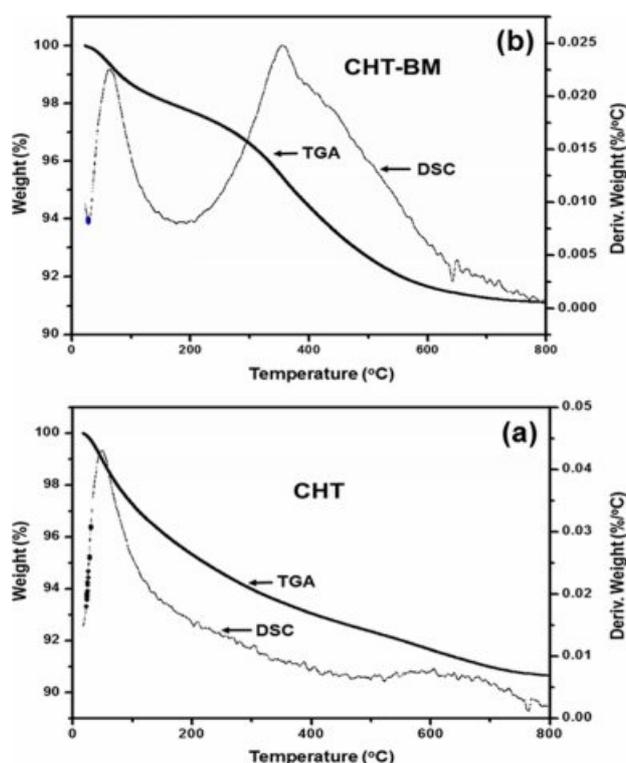


Fig. 5. TGA-DSC curves of CO₂ adsorption of Mg-Al hydrotalcite samples at 200 °C and 1 atmosphere: (a) calcined Mg-Al hydrotalcite (CHT) and (b) calcined Mg-Al hydrotalcite after ball-milling treatment for 2 h (CHT-BM).

was decreased. In general, our results clearly suggest that the agglomerate particle formation, a pore-size reduction, decreased textural properties as a consequence of the ball-milling treatment, which means that the treatment has negative effect over the CO₂ adsorption of calcined Mg-Al hydrotalcite. In that regard, these significant results, demonstrate that CHT has the potential for CO₂ capture, but that its efficiency is slightly decreased when this material is ball-milled.

Conclusions

In this study, we investigated the effect of ball-milling over the CO₂ adsorption capacity of calcined Mg-Al hydrotalcite, recognizing that this treatment is well-studied for the preparation of nanostructured materials that should improve CO₂ adsorption. However, in this work, it was demonstrated that the ball-milling process is not considered a viable alternative for the improvement of the CO₂ adsorption of calcined Mg-Al hydrotalcite, due to its high particle aggregate formation, decreased BET-surface area and pore size. Thus, based on all the aforementioned results, it was concluded that the ball-milling process does not play a crucial role in the obtainment of hydrotalcite compounds with better textural and structural properties for enhancement of CO₂ adsorption, and that the calcined Mg-Al hydrotalcite treated by ball milling for 2 h does not appear to be useful for large-scale CO₂ capture technologies, but certainly efficient when not treated by ball-milling.

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