



# High temperature CO<sub>2</sub> sorption over modified hydrotalcites



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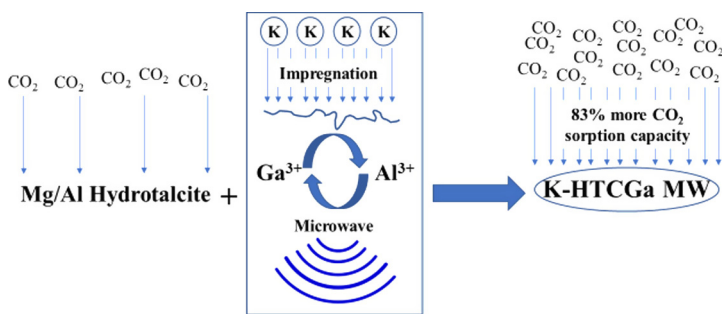
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## HIGHLIGHTS

- A K impregnated, Ga substituted microwave aged hydrotalcite was prepared.
- An astonishing CO<sub>2</sub> sorption capacity of 2.09 mol/kg was achieved at 573 K.
- Two different kinetic contributions were identified during CO<sub>2</sub> uptakes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Hydrotalcite-like materials were prepared by the co-precipitation method, characterized by PXRD, FTIR, physical adsorption of N<sub>2</sub> at 77 K and SEM/EDS, and after calcination they were tested for CO<sub>2</sub> sorption at 573 K under dry conditions. The simultaneous effect of aluminum partial substitution with gallium, microwave aging of the precipitated gel and modification with potassium on their sorption capacity was assessed. Sorption isotherms were well described by the Freundlich model for all samples. A remarkable sorption capacity of 2.09 mol/kg at 3.10 bar was obtained for the Ga-containing sample, aged under microwave irradiation and impregnated with 20 wt% of potassium. The sorption kinetics was analyzed from uptake measurements and two distinct contributions (related to fast and slow uptakes), which are considered by the proposed model, were observed. Despite the slower sorption kinetics on the potassium-modified samples, they showed sorption capacities considerably higher than those reported in the literature for commercial hydrotalcites under similar conditions, even for prolonged exposition to CO<sub>2</sub>.

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## 1. Introduction

Increasing greenhouse gases (GHG) emissions are a major concern due to the changes that they are causing on our planet environment. Most of the countries are making a collective effort in order to implement measures that will hopefully, together with other initiatives, allow to keep the increase in global average temperature less than 2 °C above pre-industrial levels. In fact, world

governments have recently (December 2015) agreed at the Paris Climate Conference to aim to limit this increase to 1.5 °C since it would considerably reduce the risks associated to impacts on climate change [1]. To achieve this target, release of carbon dioxide (one of the most emitted GHG) to the atmosphere should be sharply reduced. Moreover, and from an economical point of view, if recovered CO<sub>2</sub> can be used as feedstock for industrial production processes, the existing resource base would be broadened [2].

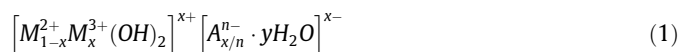
Regarding the pre-combustion capture of CO<sub>2</sub>, several processes such as absorption, sorption, chemical looping combustion, membrane separation, hydrate based separation and cryogenic

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distillation, are possible [3]. Although absorption is the most widely used CO<sub>2</sub> separation technology due to its high efficiency and lower cost [3], it is not compatible with an intensified process where, for instance, both high temperature reaction (e.g., steam reforming, water-gas shift, etc.) and CO<sub>2</sub> separation occur simultaneously. However, capture of CO<sub>2</sub> through high temperature sorption on a solid material is highly compatible with such processes. In this regard, several materials such as CaO-based materials [4,5], hydrotalcites [6,7], lithium zirconates [8,9] and lithium silicates [10,11], among others, have been reported in the literature for high temperature CO<sub>2</sub> sorption. Among these materials, hydrotalcite-related materials have been observed to be the best option for temperatures between 573 and 773 K [6,7,12–14].

Hydrotalcite is a layered double hydroxide (LDH) which structure can be considered derived from that of brucite, Mg(OH)<sub>2</sub>, and which general formula can be written as:



where M<sup>2+</sup> and M<sup>3+</sup> are divalent (e.g., Mg<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, etc.) and trivalent (e.g., Al<sup>3+</sup>, Ga<sup>3+</sup>, Mn<sup>3+</sup>, Y<sup>3+</sup>, Fe<sup>3+</sup>, etc.) metal cations within the brucite-like layers, A<sup>n-</sup> is a charge compensating anion (e.g. CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, etc.) located in the interlayer space and *x* is generally between 0.2 and 0.4 [15]. Regarding *y*, it represents the number of moles of water in the interlayer space. The mineral known as hydrotalcite possesses Mg<sup>2+</sup>, Al<sup>3+</sup> and CO<sub>3</sub><sup>2-</sup> as divalent and trivalent cations and balancing anion, respectively. However, the properties of hydrotalcites can be tailored by combining adequate cations and anions [16,17], by varying the M<sup>2+</sup>/M<sup>3+</sup> molar ratio (related to the value of *x*) [18], by modifying the hydrotalcite with alkaline metal cations (e.g. K<sup>+</sup>, Cs<sup>+</sup>, Na<sup>+</sup>, etc.) [14,19,20], by changing the synthesis conditions such as pH [16,21], aging process (e.g. conventional, microwave, ultrasonication, etc.) [6,22], or calcination temperature [19,23], among other parameters or conditions. Hydrotalcites have been reported to show good sorption capacity, stability and easy regeneration by temperature or pressure swing [14,24–26]. Moreover, it is clear by now that the presence of steam, which is common in pre-combustion applications like sorption-enhanced steam reforming, highly benefits the sorption of CO<sub>2</sub> on these materials [14,27,28].

From the literature, it is concluded that potassium modified hydrotalcites showed the best performance among several alkali-modified hydrotalcites [13–14], and that partial substitution of aluminum with gallium [13,26] also improved the performance for CO<sub>2</sub> sorption. On the other hand, the beneficial role of microwave treatment on the properties of hydrotalcites has been also reported [6,22]. Taking into account these facts, a gallium substituted Mg-Al-hydrotalcite aged under microwave irradiation and modified with potassium was evaluated in terms of CO<sub>2</sub> sorption capacity and compared to other formulations. In particular, the effects of the aluminum partial substitution with gallium, the microwave aging of the precipitated gel and the modification with potassium were separately assessed. Besides the physicochemical characterization of the synthesized materials, the sorption equilibrium isotherms at 573 K (typical temperature found in both pre- and post-combustion streams) were recorded. Finally, the sorption kinetics on the prepared materials was determined.

## 2. Experimental

### 2.1. Chemicals and gases

Aluminum nitrate 9-hydrate, magnesium nitrate 6-hydrate and gallium nitrate hydrate (Sigma Aldrich, highest purity degree available) were used as Al, Mg and Ga precursors, respectively. In order

to assure that the charge compensating anion was carbonate and not nitrate, an excess of anhydrous sodium carbonate (Sigma Aldrich, highest purity degree available) was used. Sodium hydroxide (Sigma Aldrich, highest purity degree available) was used to maintain an alkaline pH during synthesis. Potassium carbonate (Sigma Aldrich, highest purity degree available) was used as chemical promoter to modify the prepared hydrotalcites. Carbon dioxide (99.99%), nitrogen (99.999%) and helium (99.999%) used were from L'Air Liquide.

### 2.2. Preparation of the materials

Two fresh base materials were prepared: Mg<sub>2</sub>Al(OH)<sub>6</sub>(CO<sub>3</sub>)<sub>0.5</sub>·yH<sub>2</sub>O and Mg<sub>2</sub>(Al<sub>0.9</sub>Ga<sub>0.1</sub>)(OH)<sub>6</sub>(CO<sub>3</sub>)<sub>0.5</sub>·yH<sub>2</sub>O, herein named as fHTC and fHTCGa, respectively. For both materials, the Mg<sup>2+</sup>/Al<sup>3+</sup> and Mg<sup>2+</sup>/(Al<sup>3+</sup> + Ga<sup>3+</sup>) molar ratios of 2 were used and an Al<sup>3+</sup>/Ga<sup>3+</sup> ratio of 9 was used to prepare sample fHTCGa. These ratios were chosen taking into account the results previously reported by Miguel et al. [13].

The materials were prepared via the co-precipitation method: a portion of 100 ml of a solution containing the salts of the divalent (1.93 M and 1.89 M for non-containing and containing gallium samples, respectively) and trivalent cations (0.97 M and 0.95 M for non-containing and containing gallium samples, respectively) was added drop-wise to a basic solution containing NaOH (1 M) and Na<sub>2</sub>CO<sub>3</sub> (0.089 M). The final mixture was continuously stirred for approximately 20 h at room temperature. This allowed obtaining gels of the two aforementioned base materials. Then, half of the amount of fHTC and all fHTCGa suspensions were hydrothermally treated at 373 K in a Milestone Ethos Plus microwave furnace with a power of 600 W during 1 h, in sealed 100 ml Teflon reactors (fresh samples obtained are herein respectively called fHTC MW and fHTCGa MW). The heating ramp from room temperature up to 373 K was in all cases 10 K/min and the heating process was programmed with Software Easywave. After this treatment the suspensions were centrifuged and the solids were washed with distilled water to remove nitrate and sodium counterions. The samples were dried at 313 K in air, crushed and a small amount of each sample was calcined at 673 K for 2 h in air. The loss of mass during calcination of each sample was assessed in order to further prepare the potassium modified samples with a pre-determined stoichiometry. Then, half of the amount of the remaining fHTC, all fHTC MW and all fHTCGa MW were impregnated with a solution of potassium carbonate dissolved in the minimum possible amount of water with the aim of achieving a final potassium loading of 20 wt%, which is the percentage typically found in other works [6,13,29]. Finally, the samples were dried once again at 313 K, crushed, and calcined at 673 K for 2 h in air. It has been observed that calcination of hydrotalcite-based materials at 673 K allows the attainment of higher sorption capacities [30]. A summary of the prepared calcined samples that were submitted to CO<sub>2</sub> sorption tests is given in Table 1.

### 2.3. Characterization of the materials

The powder X-ray diffraction (PXRD) patterns were recorded using non-oriented powder samples, in the 2–75° 2θ range, at a scanning speed of 2° min<sup>-1</sup>. The instrument used was a Siemens D-5000 diffractometer, operating at 40 kV and 30 mA, with filtered Cu Kα radiation (λ = 1.5418 Å). The Fourier Transformed Infrared (FTIR) spectra were recorded in the 4000–450 cm<sup>-1</sup> range in a Perkin-Elmer Spectrum-One spectrometer. About 1 mg of sample and 300 mg of KBr were used in the preparation of the pellets. Nitrogen adsorption-desorption at 77 K were recorded, after degassing the samples for 2 h at 383 K in a FlowPrep 060 accessory

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