

## Effect of interlayer anion on the CO<sub>2</sub> capture capacity of hydrotalcite-based sorbents

Cláudio Rocha<sup>1</sup>, Miguel Soria<sup>1</sup>, Luís M. Madeira<sup>1\*</sup>

<sup>1</sup> LEPABE, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

\*Corresponding author: [mmadeira@fe.up.pt](mailto:mmadeira@fe.up.pt)

### Highlights

- Hydrotalcites with different interlayer anions were tested as CO<sub>2</sub> sorbents.
- Interlayer anion affects the CO<sub>2</sub> sorption capacity of hydrotalcites-based sorbents.
- Interlayer anion affects the stability of sorbents in the breakthrough cycling tests.
- The hydrotalcites-based sorbents seem promising for sorption-enhanced steam reforming.

### 1. Introduction

CO<sub>2</sub> emissions are a major environmental problem due to the changes that they are causing on our planet, increasing the global warming. In this regard, there is a great interest in developing technological solutions for large-scale CO<sub>2</sub> capture, sequestration or utilization [1]. Depending on the operating temperature, several sorbents may be used to capture CO<sub>2</sub>. It has been reported that hydrotalcites (HTCs) exhibit a good sorption capacity, stability and easy regeneration [1]. HTCs are layered double hydroxides, which general formula is  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{x/n}^{n-} \cdot y\text{H}_2\text{O}]^{x-}$ , where M<sup>2+</sup> is a divalent metal cation and M<sup>3+</sup> is a trivalent metal cation. A<sup>n-</sup> is a charge balancing anion located in the interlayer space and x is generally between 0.2 and 0.4 [1, 2], while y is the number of moles of water located in the interlayer space. Although similar layered structures of HTCs could be produced with several compensating anions, it was found that physicochemical properties are highly influenced by these anions. Additionally, it was concluded that K<sub>2</sub>CO<sub>3</sub> modified HTCs showed best performance and that partial substitution of Al with Ga also improved the performance for CO<sub>2</sub> sorption [1, 2]. In this work, besides the physicochemical characterization of the materials (commercial and prepared by us with compensating anions never used before), the sorption equilibrium isotherms were recorded. Also, the effect on CO<sub>2</sub> sorption capacity caused by Ga partial substitution and modification with K<sub>2</sub>CO<sub>3</sub> was evaluated for some samples and compared to that shown by the original HTC (for the first time for several HTCs). Finally, several of the most promising materials were also submitted to breakthrough cycling tests at 300 °C. The aim of this work was to study the potential of several sorbents to be applied in a sorption-enhanced steam reforming process.

### 2. Methods

HTCs with molar ratios Mg/Al=2 or Mg/(Al+Ga)=2 (Al/Ga=9) were synthesized using a co-precipitation method. A series of HTCs-A samples with different anions (A=CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, BrO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> or (CH<sub>3</sub>COOH)<sub>3</sub>BH<sup>-</sup>) were prepared by adding a Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and a Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution drop-wise into a anion precursor solution. The pH of the precipitation was controlled at 9.5 using a 1 M NaOH solution. After, the mixture was stirred for 20 h at room temperature and filtered. Then, the solid was washed and dried (48 h at 40 °C). The HTCs with partial substitution of Al by Ga (herein called HTC-A(Ga)) were prepared using the same procedure. Some of the dry HTCs were impregnated with a solution of K<sub>2</sub>CO<sub>3</sub> (HTC-A\_K or HTC-A(Ga)\_K) with the aim of achieving a final K loading of 20 wt.%. These materials were dried again (48 h at 40 °C). To obtain a HTC-based sorbent the respective dry HTC was calcined (2 h at 400 °C in air). The physicochemical characterization of the materials was realized through several techniques. The CO<sub>2</sub> sorption capacities were assessed using a magnetic suspension balance; CO<sub>2</sub> breakthrough runs were carried out with a sorption step (with a feed of 15 vol.% of CO<sub>2</sub> balanced in N<sub>2</sub>) and a regeneration step carried out under N<sub>2</sub> flow at 300 °C.

### 3. Results and discussion

The CO<sub>2</sub> sorption capacities of calcined HTCs (prepared by us) at 300 °C for different partial pressures of CO<sub>2</sub> are shown in Figure 1. Among the HTCs-A prepared, HTC-CO<sub>3</sub> showed the highest CO<sub>2</sub> capture

capacity of 1.08 mmol/g ( $P_{\text{CO}_2} = 1$  bar), which was much higher than other HTCs. Almost all experimental data of  $\text{CO}_2$  sorption isotherms present a good fitting to the Freundlich model. It was verified that the Ga partial substitution in the  $\text{HTC-CO}_3$  enhanced the sorption capacity (1.15 mmol/g for  $\text{HTC-CO}_3(\text{Ga})$  at  $P_{\text{CO}_2} = 1$ ) and by doping this HTC with 20 wt.% K ( $\text{HTC-CO}_3\text{-K}$ ), the  $\text{CO}_2$  sorption capacity was increased up to 1.43 mmol/g ( $P_{\text{CO}_2} = 1$  bar). These effects were not observed for  $\text{HTC-(CH}_3\text{COOH)}_3\text{BH}^-$  (sorption capacity increases with the impregnation of K and decreases with the Ga partial substitution). However, from the stability cycling tests it was observed that the  $\text{HTC-(CH}_3\text{COO)}_3\text{BH}^-$  sample reaches the working capacity in the second breakthrough test and so presents high stability (capacity decreased only 9 %), while most samples had a worse stability performance.

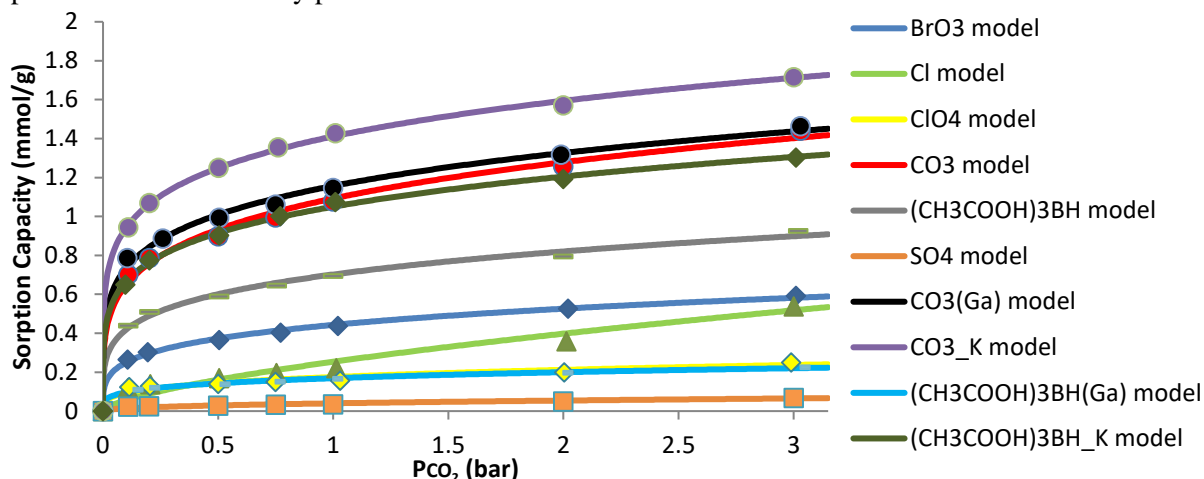


Figure 1.  $\text{CO}_2$  sorption isotherms at 300 °C and fitting with the Freundlich model.

#### 4. Conclusions

This work reports a detailed investigation on how the compensating anion affects the structural properties and  $\text{CO}_2$  sorption capacity of HTCs-based sorbents. It was found that the anions have an effect on the thermal stability and morphology, modifying the  $\text{CO}_2$  capture capacity of the sorbents. Among these HTCs,  $\text{HTC-CO}_3$  showed the highest  $\text{CO}_2$  sorption capacity of 1.08 mmol/g ( $P_{\text{CO}_2} = 1$  bar). By doping  $\text{HTC-CO}_3$  with 20 wt.% K, the  $\text{CO}_2$  adsorption capacity was further increased, up to 1.43 mmol/g ( $P_{\text{CO}_2} = 1$  bar) and it was verified that the Ga partial substitution in this HTC also enhanced the sorption capacity (1.15 mmol/g at  $P_{\text{CO}_2} = 1$  bar). Nevertheless, it was found that the  $\text{HTC-(CH}_3\text{COO)}_3\text{BH}^-$  presents the higher stability in the breakthrough cycles. Some of the sorbents prepared present a very good performance to be subsequently used in a sorption-enhanced steam reforming process.

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#### Keywords

Hydrotalcite, Anion effect;  $\text{CO}_2$  capture capacity; Sorption.