# Synthesis of layered double hydroxides from an industrial waste for $CO_2$ adsorption at moderate temperatures

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## *Introduction*

Curving the $CO_2$ atmospheric levels is one of the challenges of this century, given its direct impact on climate change. Of the several strategies of $CO_2$ capture and storage, sorption-enhanced water–gas shift (SEWGS) process, a combination of $CO_2$ adsorption and the water–gas shift reaction, has been appointed as one of the most promising techniques due to is low energy consumption and high efficiency. SEWGS operating settings at both moderate temperature (200–450 °C) and high pressure (more than 10 bar) bring the need to find an adsorbent capable of working at these conditions. Calcined layered double hydroxides (LDH) have been proven to give the best results in this range of pressure/temperatures even though its performance can be greatly improved. Their surface modification with potassium has been proven to boost its adsorption capacity (see Figure 1). Herein, Layered double hydroxides with different metal composition $M^{2+}$ (cobalt, magnesium, nickel and zinc) were synthesized using always aluminum extracted from a saline slag, a hazardous waste generated during the recycling process of aluminum. Their $CO_2$ adsorption capacity in a wide range of temperatures (between 50 and 400 ºC) is reported. The effect of either the divalent cation is evaluated, as well as the modification of the surface properties by the incorporation of K from two sources, $K_2CO_3$ and KOH. In addition, the samples modified with KOH have been functionalized with an amine tetraethylenepentamine (TEPA) to test the adsorbent capacity in post-combustion conditions (up to 100 ºC).

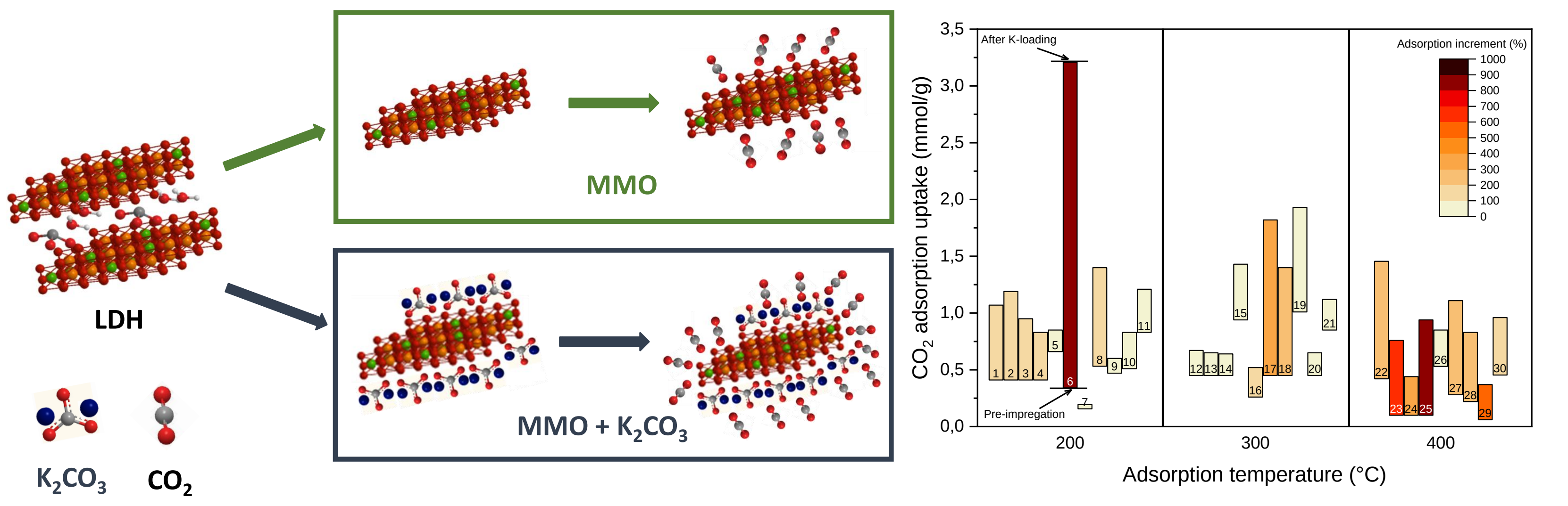

**Figure 1.** Increment on the $CO_2$ adsorption capacity when impregnated with $K_2CO_3$ (doi:10.1016/j.cej.2022.140551)

## *Hydrotalcite-like compounds synthesis, modifications and characterization*

Al* was extracted from aluminum saline slags using the following procedure: 5 g of saline slag were added to 100 mL of an aqueous reagent solution (NaOH 2 mol/L) in a reflux system, stirred at 500 rpm and heated to 373 K for 60 min. The slurries were separated by filtration and the aluminum concentration in the solution was determined by ICP-OES and found to be 7.03 g/L. The $M^{2+}/M^{3+}$ chosen ratio was 3:1 using either cobalt, magnesium, nickel or zinc as $M^{2+}$ and $Al^{3+}$ from saline slags as $M^{3+}$. In the synthesis method used, an aqueous solution of $M^{2+}$ and the $Al^{3+}$ extracted were dropwise added to an aqueous solution of $Na_2CO_3$ to a final volume of 400 mL, NaOH was used during the process to adjust the pH to 10. The mixture was stirred at 500 rpm and 60 ºC for 60 min and aged for 24 h. The slurries obtained were centrifugated at 8000 rpm for 5 min and washed. This process was repeated several times until the washing water achieved a pH of 7. The samples were then dried at 80 ºC for 16 h, manually grounded with a mortar and calcined at 400 ºC for 4 h.

**$K_2CO_3$ Impregnation procedure**:
$M_6Al_2$ were impregnated with 15 wt. % $K_2CO_3$ using an incipient wetness method. In order to obtain 15 wt. % loading, an aqueous solution (1.5 mL) containing 0.088 g of $K_2CO_3$ was added to 0.5 g of $M_6Al_2$ to the point of incipient wetness. The resulting paste was dried at 120 °C for 16 h and then calcined at 400 °C for 4 h.

**KOH impregnation procedure:**
1 g of calcined $M_6Al_2$ was dispersed in 0.1 mol/L KOH in ethanol and stirred at 120 rpm for 30 min. The samples were then washed with ethanol several times and finally dried for 10 h at 60 °C and atmospheric pressure.

**TEPA impregnation procedure**:
Half the amount obtained previously was separated and impregnated with TEPA at a 40/60 TEPA/$M_6Al_2$+KOH proportion. The steps followed were: first, a mixed solution of TEPA/ethanol at a constant mass to volume ratio of 1/2 was prepared and then was added to the $M_6Al_2$ + KOH samples and stirred for 30 min at 120 rpm. A slurry was obtained after a drying step of 1 h at 60 °C and the final adsorbent was collected after a 10 h drying process at 90 °C.

The PXRD patterns of the fresh and calcined $M_6Al_2$ LDH and also impregnated $M_6Al_2+K_2CO_3$ and $M_6Al_2$+KOH are summarized in **Figure 2**. $Co_6Al_2$ sample shows the crystal structure of the $Co_3O_4$ spinel. The impregnation of the sample with KOH or $K_2CO_3$ did not display any new peaks but the same peaks with less definition, peaks at 59° and 65° are less defined and blurred together in KOH sample. The $Mg_6Al_2$ sample presents the periclase crystal structure of MgO when calcined. Samples impregnated with potassium show the periclase peaks together with a peak at 11°, revealing the rehydration of the structure (as is the main peak (003) of the LDH) and a series of small peaks between 25 and 35 2θ degrees in the carbonate sample, typical of $K_2CO_3$. In the $Ni_6Al_2$ sample nickel oxide (NiO) was formed and the $Zn_6Al_2$ sample was transformed into zincite (ZnO) when calcined. In both cases a different structure can be appreciated only in the carbonate impregnation, with a peak appearing at ~15° and a group of peaks at between 25 and 35°.

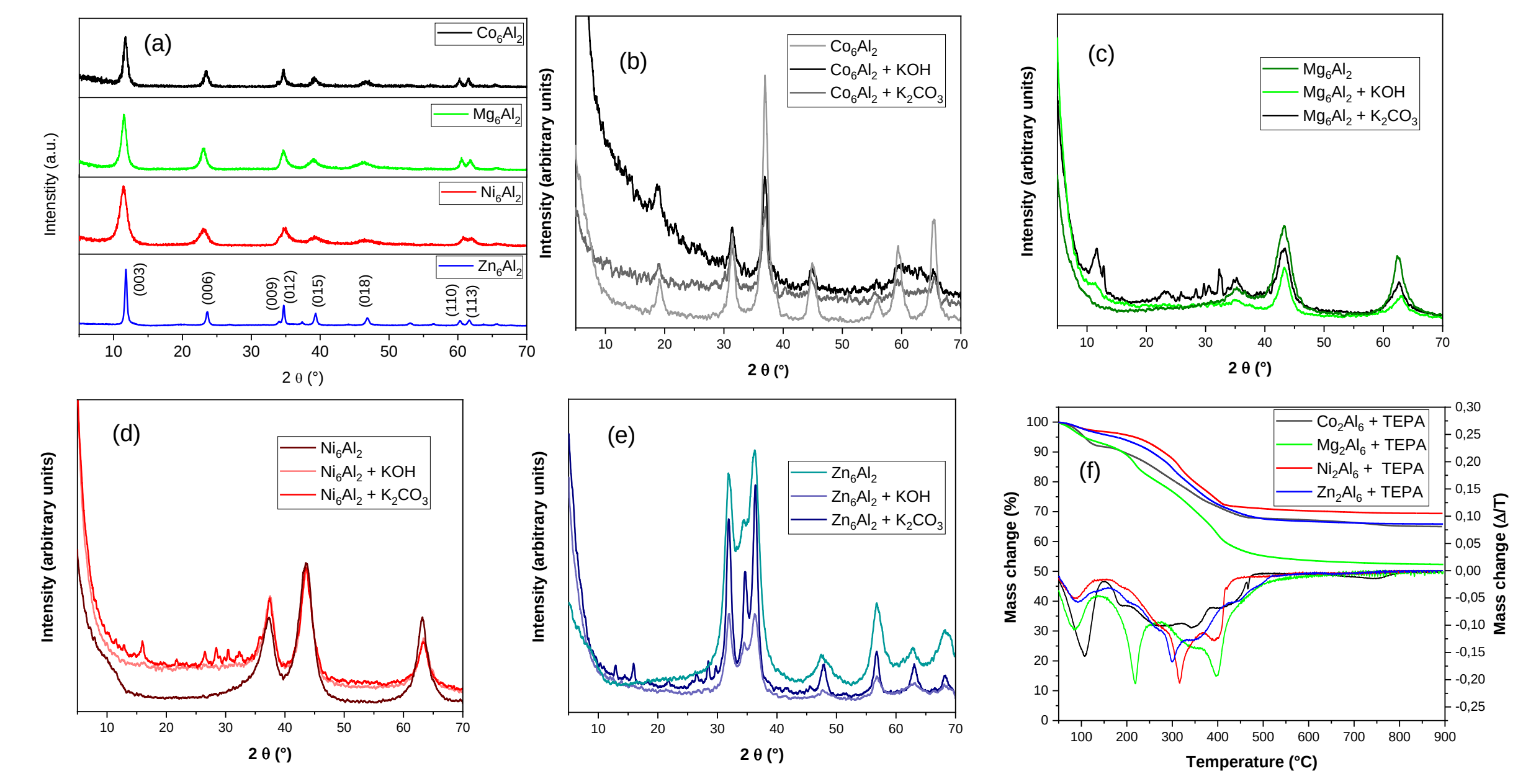

**Figure 2.** Powder X-ray diffraction patterns of the non-calcined **(a)** and calcined samples (without modification and modified with KOH or $K_2CO_3$) with either cobalt **(b)**, magnesium **(c)**, nickel **(d)** and zinc **(e)** as $M^{2+}$.**(f)** TG and DTG curves of the $M_6Al_2$+KOH+TEPA series.

Thermal analysis of the $M_6Al_2$+KOH+TEPA samples was performed in order to analyze the thermal stability of the samples impregnated with TEPA and thus select the maximum temperature of the $CO_2$ adsorption experiments of these samples. The decomposition behavior of TEPA appears between 120 and 260 °C preceded by a small 3% water loss at lower temperature. The thermogravimetric analysis (upper lines) and differential thermal analysis (lower lines) results obtained for the four samples are displayed in **Figure 2f**. All the samples have a first step at around 100 °C, bigger in the case of cobalt and magnesium samples, which is assigned to the loss of loosely bound water and gases. From 250 to 450 °C the second major loss occurs which corresponds to the loss of TEPA. In some samples, like nickel, this loss is divided into two steps. Surface interactions of the impregnated TEPA onto $M_6Al_2$+KOH samples have a delaying effect on the TEPA degradation of more than 100 °C.

## Conclusions

This study gives an insight of the overall performance of calcined LDH synthesized from aluminum slags when subjected to several modification strategies ($M^{2+}$ and surface modification) in an attempt to boost its $CO_2$ adsorption capacity at both low and moderate temperatures. Calcined LDH with aluminum extracted from saline slags and a $M^{2+}/M^{3+}$ ratio of 3:1 were tested as adsorbents over a range of temperatures for pre-combustion (200 – 450 ºC) and post-combustion (< 100 °C) $CO_2$ capture. Cobalt, magnesium, nickel and zinc are tested as $M^{2+}$, with nickel-containing calcined LDH having the best adsorption capacity at lower temperatures followed by $Mg_6Al_2$.The latter maintains the adsorption capacity in the moderate-temperature range, performing better than the commercial sample at pre-combustion temperatures. Surface modification with KOH or $K_2CO_3$ give various effects; while KOH improves usually the adsorption capacity of the samples, $K_2CO_3$ impregnation tends to work better at higher temperatures, giving the best overall result on the $Mg_6Al_2$ sample (0.58 $mmol_{CO2}$/g). This sample, $M_6Al_2+K_2CO_3$ was tested in a series of adsorption-desorption cycles at 400 °C using the pressure swing approach and its working capacity was found to be 0.50 $mmol_{CO2}$/g. $M_6Al_2$+KOH samples were impregnated with the amine TEPA in with the aim of improving their performance at post-combustion conditions, obtaining good results for cobalt and magnesium samples.

References:

L. Santamaría, S.A. Korili, A. Gil, Layered double hydroxides for $CO_2$ adsorption at moderate temperatures: Synthesis and amelioration strategies, Chem. Eng. J. 455 (2023) 140551. https://doi.org/https://doi.org/10.1016/j.cej.2022.140551.

L. Santamaría, S.A. Korili, A. Gil, Metal-Al layered double hydroxides synthesized from aluminum slags as efficient CO2 adsorbents at pre- and post-combustion temperature, J. Environ. Chem. Eng. 11 (2023) 110936. https://doi.org/10.1016/j.jece.2023.110936.

## *$CO_2$ adsorption experiments*

The $CO_2$ adsorption isotherms obtained at 50 and 400 ºC of the calcined LDH with different $M^{2+}$ (Co, Mg, Ni and Zn) are summarized in **Figure 3**. At 50 ºC the sample $Ni_6Al_2$ is the solid with the highest adsorption capacity, followed by $Mg_6Al_2$, $Co_6Al_2$ and $Zn_6Al_2$, which has the lowest capacity. Both $Ni_6Al_2$ and $Mg_6Al_2$ are characterized by their significant adsorption capacity at low pressures. When considering the moderate temperature range 200-400 °C, more adequate for pre-combustion application, $Mg_6Al_2$ offers the best results with a maximum adsorption capacity of 0.275 mmol/g. At 400 ºC, it can be seen how $Mg_6Al_2$ maintains its adsorption capacity, while the other materials suffered a significant reduction in theirs. The maximum values found in these cases are 0.136 ($Ni_6Al_2$), 0.088 ($Co_6Al_2$) and 0.074 $mmol_{CO2}$/g ($Zn_6Al_2$).

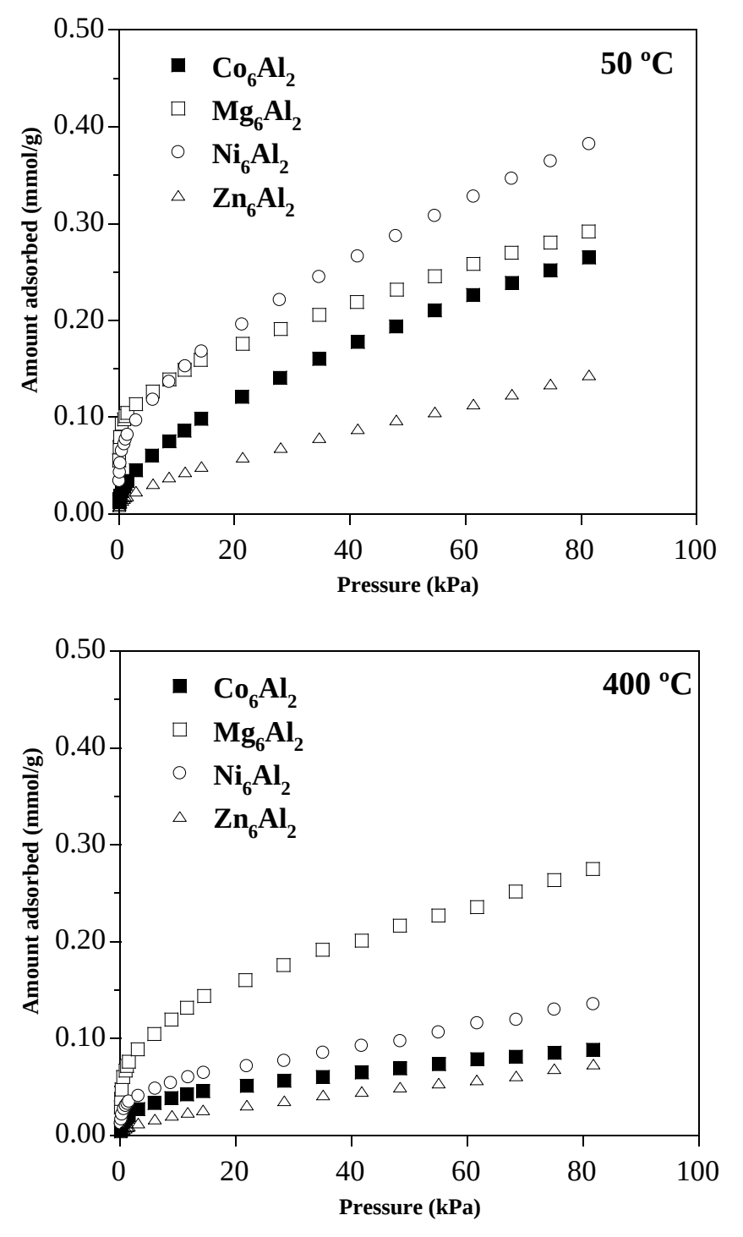

**Figure 3**. Comparison of the $CO_2$ adsorption capacity of the different non-impregnated samples at 50 and 400 °C.

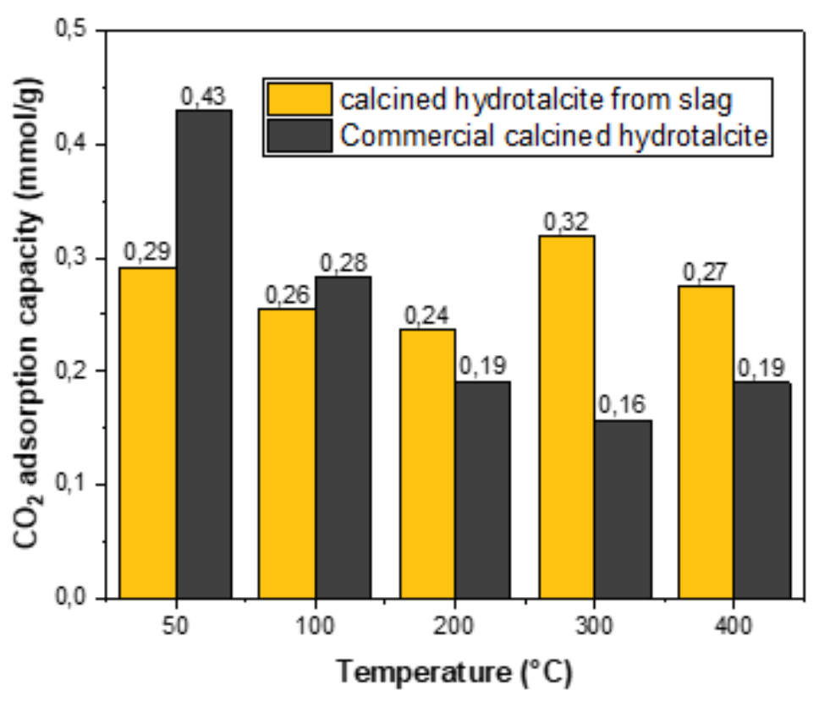

**Figure 4.** $CO_2$ – adsorption capacity differences between a commercial sample $Mg_6Al_2$ and that synthesized from saline slags.

As $Mg_6Al_2$ sample provided the greatest outcome, this sample adsorption capacity was compared to that of a commercial hydrotalcite (also with a Mg/Al ratio of 3/1 and calcined at 400 °C for 4 h). The results at several temperatures and 80 kPa pressure are represented in **Figure 4**. The commercial $Mg_6Al_2$ seems to reduce its capacity as the temperature increases and has the best result at 50 °C. The $Mg_6Al_2$ synthesized from slag has more potential in the range of pre-combustion-working temperature as its best capacity is obtained at 300 °C.

The adsorption results of the samples modified with potassium (either KOH or $K_2CO_3$) and TEPA are represented in **Figure 5**. The experiments performed at 50 ºC show that the best results are obtained by $Co_6Al_2$ and $Mg_6Al_2$, specially with the TEPA-functionalized samples (maxima adsorption capacity up to 80 kPa: 0.450 and 0.456 $mmol_{CO2}$/g). At this range of temperature KOH works better than $K_2CO_3$, in fact the latter reduces the adsorption capacity of the non-modified samples in three cases, as the alkalinity boost that provides $K_2CO_3$-impregnation does not seem to compensate the severe loss of available surface. At 400 °C $Mg_6Al_2$ gives the best results ($Mg_6Al_2$-$K_2CO_3$, 0.58 $mmol_{CO2}$/g).

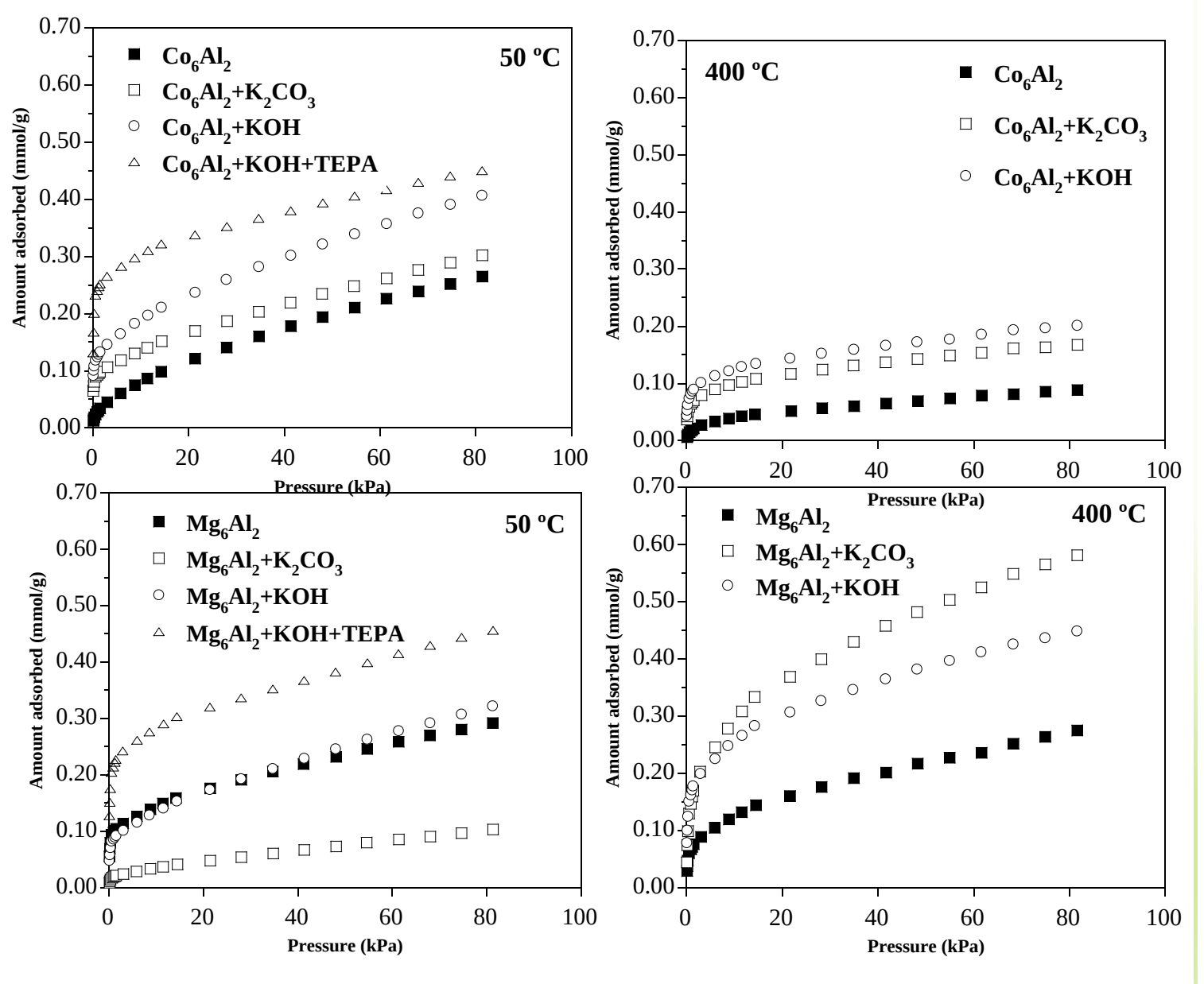

**Figure 5**. Comparison of the $CO_2$ adsorption capacity of the impregnated $Co_6Al_2$ and $Mg_6Al_2$ at 50 and 400 °C.

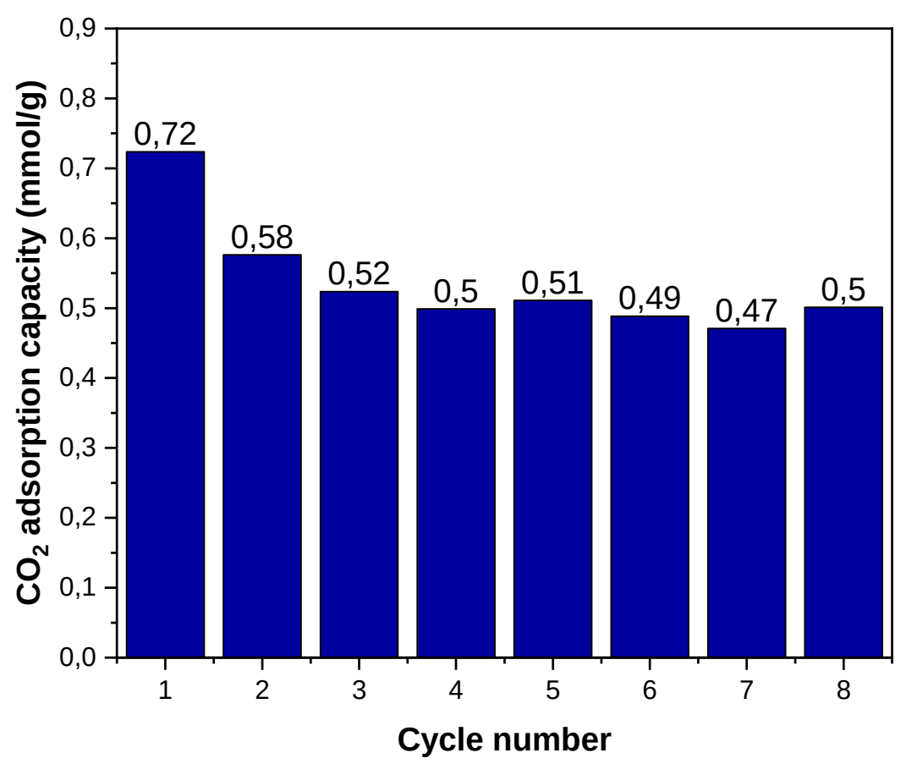

**Figure 6.** $CO_2$ – adsorption capacity of $K_2CO_3$-modified MgAl LDH at 400 °C over a series of cycles.

Having the best results, $K_2CO_3$-impregnated $Mg_6Al_2$ adsorption capacity was put to the test in a series of adsorption-desorption cycles at 400 °C using the pressure swing approach, as is faster and more energy-efficient. Results obtained are presented in **Figure 6**. The initial adsorption capacity in the first cycle (0.72 $mmol_{CO2}$/g) is reduced to 0.58 $mmol_{CO2}$/g in the second cycle and later stabilizes at around 0.50 $mmol_{CO2}$/g for the next 6 cycles, which could be considered its working capacity. The initial drop is due to the fraction of adsorbate that is irreversibly chemisorbed and thus, cannot be easily removed.

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