

Effect of the surface properties of Me^{2+}/Al layered double hydroxides synthesized from aluminum saline slag wastes on the adsorption removal of drugs

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ABSTRACT

This work presents the synthesis of Me^{2+} (Co, Mg, Ni and Zn)/Al layered double hydroxides (LDH) with a 3:1 M ratio by the co-precipitation method. Structural characterization and comparison of the series has been achieved using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), nitrogen physisorption at 77 K, thermogravimetry measurements (TGA), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), ammonia temperature-programmed desorption (NH_3 -TPD) and point of zero charge (pHpzc). Batch experiments were performed to analyze the adsorption capacity of the different LDH on diclofenac and salicylic acid, as example of emergent pollutants. The pH, mass of adsorbent, contact time and concentration of pollutant were the parameters used to compare the adsorption performance of the synthesized materials. Samples showed different behavior and the equilibrium was reached at different times, Mg_6Al_2 and Zn_6Al_2 showed lower equilibrium times but had higher adsorption capacity. Various adsorption and isotherm equation models were employed to study both the kinetic and equilibrium results and, in general, the removal of diclofenac was greater than that of salicylic acid. 1-Butanol conversion was also used as a means of acidity and basicity characterization and the results were compared with the adsorption performance of the samples in order to explain the results found. A relationship between the amount of pollutants adsorbed and the butenes formed in the dehydrogenation reaction of 1-butanol was found.

1. Introduction

Even though priority pollutants are still the main focus in wastewater treatment, an increasing attention is being given to unregulated emerging contaminants. This type of compounds (which range from pharmaceuticals, hormones and steroids to flame retardants, gasoline and industrial additives) have undesired effects on the environment and need to be monitored in the near future [1]. Several techniques can be applied and membrane processes [2], adsorption [3] and photocatalysis [4] have been proven to be amongst the most effective [5]. All of them having pros and cons adsorption is one of the most studied due to its rapid pace and low energy consumption. Even if different adsorbents such as active carbons [3], zeolites [6] or metal organic frameworks [6] have been studied in the past, a new trend towards greener adsorbents [5,6] or, like in this study, integrating hazardous waste remediation,

seems to be congruent.

The secondary aluminum smelting process generates various types of wastes of which the largest, in % by mass, are saline slags. Catalogued as hazardous wastes in European Waste List [7], they are generated because salts are added to prevent oxidation, enhance the thermal efficiency of the process and scatter the oxides present in the smelting furnace [8]. Saline slags have a significant economic value. Alas its recovering process is not cost-effective and the wastes are currently stored in controlled landfills [9] once its metal fraction has been separated. However, aluminum saline slags, as a mixture of oxides, can be used for direct applications such as road paving or inert filling for construction or even recovered as a high-value product and used to synthesize salts or alumina [10]. In this study, aluminum extracted from saline slags was used to synthesize layered double hydroxides.

Layered double hydroxides (LDH), also known as anionic clays, are

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compounds with a structure based on that of brucite $[\text{Mg}(\text{OH})_2]$ with the substitution of some Me^{2+} for Me^{3+} which creates a positive charge that is balanced by the presence of anions in the interlayer. The possibility of varying the identity and the relative proportions of the Me^{2+} , Me^{3+} and the anions in the interlayer shapes the LDH group, which follows the general formula $[\text{Me}^{2+}_{1-x}\text{Me}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n} \cdot y\text{H}_2\text{O}$. LDH is naturally formed and has a Mg/Al ratio of 3 ($x = 0.25$) although ratios between 2 and 4 ($0.2 < x < 0.33$) are found in synthetic samples. Several studies have been completed to define the limits of which metal ions can form LDH such as ionic radii [11], solubility products [12] or thermodynamic factors [13]. The most commonly used Me^{2+} cations are Co, Cr, Cu, Mg, Mn, Ni and Zn; Al and Fe are usually the Me^{3+} and the most frequent anion is CO_3^{2-} . LDH can be calcined to extract the water and anions of the interlayer and form mixed metal oxides (MMO). These MMO have multiple applications primarily as adsorbents [14] and catalysts [15]. MMO can have the ability to recover their previous LDH structure when in contact with water of whom hydroxides serve as compensating ions, in the so called *memory effect* which can be used to trap different anions in the interlayer space.

Nonsteroidal anti-inflammatory drugs (NSAIDs) are emerging contaminants and over-the-counter pharmaceutical compounds used to reduce pain, decrease fever and inflammation. Their high consumption rates together with the inability of waste-water treatment plants to efficiently remove some of them have pointed them out as excellent chemical markers of wastewater contamination [16]. Salicylic acid effects on the environment have been studied with different results [17–20] and although in general it has good removal percentages, it is usually present in surface waters [21]. Diclofenac, with a more acute ecotoxicity and lower removal rates in wastewater treatments, has been incorporated into the European Commission's watch-list of substances for monitoring in the field of water policy 2015/49 [22].

In this work LDH with various Me^{2+} (Co, Mg, Ni and Zn) and aluminum extracted from saline slags as Me^{3+} (with a 3:1 $\text{Me}^{2+}:\text{Me}^{3+}$ molar ratio) were synthesized by a modified co-precipitation method. These synthesized and calcined LDH were then studied as adsorbents of diclofenac and salicylic acid, as representative compounds of emergent pollutants. Special attention was given to the characterization of acid and basic sites of the calcined LDH to tentatively explain the adsorption performance of rehydrated LDH.

2. Experimental procedure

2.1. Materials

The materials used for the synthesis of hydrotalcites were: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Panreac, $\geq 98\%$), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99.99\%$), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Panreac, $\geq 98\%$), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), Na_2CO_3 (Sigma-Aldrich, $\geq 99.99\%$), HNO_3 was used for pH adjustment and NaOH (Panreac) for both pH adjustment and aluminum extraction. 1-butanol (Roth, $\geq 99.95\%$), ammonia (Air Liquide, 99.995%), helium (Praxair, 99.999%) and nitrogen (Praxair, 99.999%) were also used.

The following adsorbates were used without any modification: salicylic acid, (2-hydroxybenzoic acid, 2-(HO) $\text{C}_6\text{H}_4\text{COOH}$, $\geq 99.99\%$, Sigma-Aldrich) and diclofenac sodium salt (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid sodium salt, $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NNaO}_2$, Sigma-Aldrich).

2.2. Hydrotalcite-like compounds synthesis

The aluminum used was extracted from saline slags using the procedure previously reported [23]. The aluminum concentration in the solution was determined by ICP-OES and found to be $6.15 (\pm) 0.14 \text{ g/L}$.

Layered double hydroxides were synthesized by a modified co-precipitation method with a molar ratio $\text{Me}^{2+}:\text{Al}^{3+}$ of 3:1. Four samples were synthesized using cobalt, magnesium, nickel and zinc as Me^{2+} .

As an example, solutions 0.0266 mol/L of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.080 mol/L of aluminum were added dropwise to a 0.015 mol/L solution of Na_2CO_3 ; the final volume was 400 mL . Both NaOH and HNO_3 were used to adjust the pH to 10. The mixture was stirred at 333 K and 500 rpm for 1 h and then aged for 24 h . The slurries obtained in the washing water were then centrifuged (8000 rpm) and washed several times until a pH of 7 was obtained. The samples were then dried for 16 h at 353 K , manually grounded with a mortar and calcined for 4 h at 673 K (LDH with Mg was calcined at 823 K). Samples were named as Co_6Al_2 , Mg_6Al_2 , Ni_6Al_2 and Zn_6Al_2 , respectively.

2.3. Characterization techniques

Powder X-ray diffraction (PXRD) patterns were measured at room temperature with a Siemens D-5000 X-ray diffractometer using a Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) in a 2θ range from 5 to 70° and a scanning rate of $0.2^\circ (2\theta)/\text{min}$. The X-ray source was working with 40 kV of voltage and a current of 30 mA .

The morphology of the samples was analyzed by scanning electron microscopy (SEM) on a Phenomenon World, XL operating at 15 kV .

N_2 physisorption was performed at 77 K with a Micromeritics ASAP 2020 Plus adsorption analyzer. The samples (0.4 g) were degassed under vacuum before measurement at 423 K for 24 h . The specific surface area (S_{BET}) was evaluated by the BET method in the range between 0.05 and 0.20 of relative pressure. The external surface area (S_{ext}) and the micropore volumes (V_{up}) were also estimated using the *t*-plot method.

The thermogravimetric measurements (TGA) were carried out in a Hi-Res TGA2950 apparatus (TA-Instruments). The samples were heated up from room temperature to 1173 K with a 10 K/min heating rate under a dry air atmosphere (60 mL/min).

Temperature-programmed reduction (TPR) studies were performed on a Micromeritics TPR/TPD 2900 instrument under a 30 mL/min flow of $5\% \text{ H}_2$ (H_2/Ar , Praxair) carrier gas. A cold trap was used to retain compounds formed during the precursor decomposition, thus avoiding possible interferences with the measured signal.

X-ray photoelectron spectroscopy (XPS) analyses were carried out on a SSX 100/206 spectrometer for Surface Science Instruments (USA) equipped with a monochromatized and microfocused Al X-ray source (powered with 20 mA and 10 kV). The pressure within the analysis chamber was about 10^{-6} Pa . The zone analyzed was about 1.4 mm^2 , and the pass energy was set at 150 eV for the general spectra and at 30 eV for the elementary spectra. An electron gun set at 8 eV and a nickel grid placed 3 mm above the surface of the samples were used to stabilize the charge. The surface adventitious carbon peak, $\text{C } 1s$ at 284.8 eV , was used as a reference for all the binding energies. When required, spectra were decomposed with the CasaXPS program (Casa Software Ltd., UK) with a Gaussian/Lorentzian product function after subtraction of a nonlinear baseline.

NH_3 adsorption and subsequent temperature-programmed desorption (NH_3 -TPD) were carried out in a Hidden CATLAB-PCS combined microreactor and mass spectrometer (MS) system equipped with a quadrupole. Three steps were followed to perform the experiments: (1) stabilization of a flow of pure Ar (30 mL/min) at 323 K for 25 min in order to check the sensitivity factor of Ar and therewith to determine that of NH_3 during the later TPD (through the previously calibrated Ar/ NH_3 sensitivity factors ratio) and subsequent heating to 673 K (still under 30 mL/min of pure Ar); (2) adsorption of NH_3 at 423 K for 1.5 h from a $95:5 \text{ Ar/NH}_3$ flow (25 mL/min) mixed with a flow of pure Ar (5 mL/min); (3) flush at 423 K under pure Ar (30 mL/min) for 2.5 h in order to eliminate physisorbed NH_3 and subsequent TPD from 423 to 923 K (10 K/min , still under 30 mL/min of pure Ar) in order to desorb chemisorbed NH_3 . The amount of NH_3 desorbed allows the number of acid sites to be calculated, the desorption temperature reflects the strength of these sites.

The point of zero charge was determined with the salt addition method. A 0.01 mol/L NaCl solution was used as background

electrolyte. A background solution (50 mL) was apportioned into various flasks kept in series with increasing pH values from 2 to 12. 0.15 g of adsorbent was added to all these flasks and the change in pH of each solution was recorded after shaking the samples for 48 h. This change in pH was plotted against the initial pH values on the graph, and the PZC was identified as the pH when $\Delta\text{pH} = 0$.

2.3.1. Butanol conversion procedure

The dehydration and dehydrogenation reactions were carried out in a two-reactor system, one used as a blank with only glass balls inside (500–800 μm) and the other with 180 mg of catalyst mixed with glass balls up to a bed height of 2 cm and extra 0.5 cm of balls to homogenize the gas input. Before the reaction, catalysts were sieved, and the particle size fraction of 100–200 μm was used. The reactor was placed in a vertical furnace with temperature control. The real reaction temperature was measured by a thermocouple situated near the catalyst, in the middle part of the reactor. Sample pretreatment was made at 473 K for 2 h under a nitrogen flow (30 mL/min). After the pretreatment the reactor was heated to 373 K and nitrogen was saturated with 1-butanol vapor (Roth, $\geq 99.95\%$). The 1-butanol temperature was 337.75 K to obtain a 10% of butanol in the flow. To prevent the condensation of 1-butanol or reaction products, all lines from the saturator to the chromatograph were heated at 373 K. A first series of 6 chromatograms was performed over the blank reactor and then changed to the sample reactor to perform 6 chromatograms every 50 K from 373 K to 723 K. Unconverted 1-butanol and the dehydration and dehydrogenation products were analyzed by a Thermo Scientific Trace 1300 gas chromatograph, equipped with a FID detector. A 30 m*0.32 mm, 0.25 μm (Stabilwax) capillary column was used for the separation of the various compounds. In addition, a Hayesep column (N 60–80, 0.25 m*1/16" SS) with a TCD detector was used to quantify the nitrogen. The estimation of the initial contents of both nitrogen and butanol were made from the intensities measured in the blank chromatograms and, in the next steps, the other components signals were normalized to that of nitrogen. The conversion (%) was defined as the ratio of the amount of converted butanol to the amount of butanol detected by the blank reactor. The selectivity for each product (%) was defined as:

$$\text{Selectivity (\%)} = \frac{\text{quantity of product} \times \text{correction factor}}{(\text{butanol initial quantity} \times \text{conversion \%})}$$

The correction factor was calculated from calibration and taking into account the number of carbons of the product.

2.4. Adsorption procedure

The adsorption isotherms of diclofenac and salicylic acid were determined under batch adsorption experiments. The selection of the initial pH was made by adjusting the drug solutions (50 $\mu\text{mol/L}$) to a range of several pHs from 2 to 12 by adding HNO_3 or NaOH . 10 mg of the adsorbent were added to the beaker and shaken for 2 h at 298 K. The drug concentration in the filtered solutions (0.45 μmol , Durapore) was determined by a Jasco V-730 UV-Vis spectrometer. Maximum adsorption wavelengths used were 276 nm for diclofenac and 297 nm for salicylic acid.

The kinetic tests were performed to study both the effect of the adsorbent dose and drug concentration. The adsorbent dose was examined by using various amounts of adsorbent (15, 30 and 60 mg) in a 150 mL solution with a drug concentration of 75 $\mu\text{mol/L}$. Samples were shaken in a stirring plate throughout the duration of the experiments. The effect of the drug concentration was studied by adding 30 mg of the adsorbent to solutions with several drug concentrations (25, 50 and 75 $\mu\text{mol/L}$). Samples of the solution were taken at various time intervals until equilibrium was attained, or up to 7 h. The amount of drug adsorbed by the hydrotalcites was estimated by subtracting the initial and remaining concentrations, using the following equation:

$$q_{t,e} = \frac{V \cdot (C_0 - C_{t,e})}{m} \quad (1)$$

where C_0 ($\mu\text{mol/L}$) is the initial concentration and C_t is the concentration at a time t of the organic compound in solution, V (mL) was the volume of the solution and m (g) was the adsorbent mass. The sorption mechanism, i.e. transport of adsorbates inside the adsorbent particles was studied considering two kinetic modeling approaches: pseudo-first- and pseudo-second-order rate equations were applied using OriginPro program (version 2018) to test the experimental data.

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where q_e is the amount of adsorbed solute at equilibrium and q_t at a time t ($\mu\text{mol/g}$), k_1 is the reaction rate constant of pseudo-first-order and k_2 of pseudo-second-order.

Equilibrium studies were performed to study the hydrotalcites adsorption capacity for the two drugs as a function of the contaminant concentration. Glass tubes with 10 mL of the drug solutions at various concentrations (between 20 and 1000 $\mu\text{mol/L}$) were combined with 5 mg of adsorbent and shaken for 7 h. As in kinetic studies, drug concentrations of the filtered samples were estimated with UV-visible

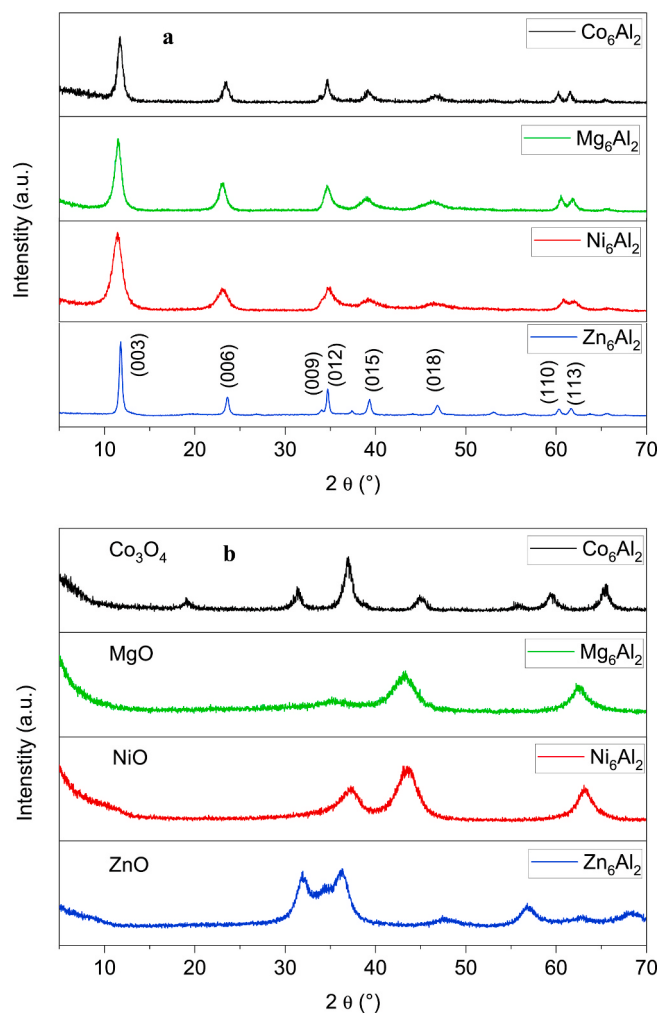


Fig. 1. Powder X-ray diffraction patterns of non-calcined (a) and calcined samples (b).

Table 1Diffraction positions, crystallite size, *c* and *a* parameters of the non-calcined LDH samples.

Sample	<i>d</i> ₍₀₀₃₎ (nm)	<i>d</i> ₍₀₀₆₎ (nm)	<i>c</i> (nm)	<i>d</i> ₍₁₁₀₎ (nm)	<i>a</i> (nm)	Crystallite size (nm)
Co ₆ Al ₂	0.759	0.380	2.282	0.155	0.309	12.9
Mg ₆ Al ₂	0.765	0.386	2.307	0.153	0.307	9.5
Ni ₆ Al ₂	0.775	0.387	2.323	0.153	0.305	6.7
Zn ₆ Al ₂	0.752	0.378	2.263	0.154	0.308	30.3

spectrophotometry and using Eq. (1) (C_e , in $\mu\text{mol/L}$, was the drug concentration at equilibrium).

The equilibrium experimental data obtained were used to better define the interactive behavior between solutes and adsorbents. Several models can be considered for that purpose. In our study we used Langmuir (Eq. (4)) and Freundlich (Eq. (5)) two-parameter isotherms and Toth (Eq. (6)) three-parameter isotherm. Langmuir isotherm assumes homogeneous and monolayer adsorption, with each molecule possessing constant enthalpy. Freundlich isotherm studies processes that happen in heterogeneous surfaces and defines the exponential distribution of the surface active sites. The Toth isotherm is an empirical modification of both the Langmuir and Freundlich equations which tries to reduce the difference between experimental data and predicted value of equilibrium data. This model is most useful in describing heterogeneous adsorption systems under both low and high end boundaries of adsorbate concentration [24].

$$q_e = \frac{k_L \cdot q_L \cdot C_e}{1 + k_L \cdot C_e} \quad (4)$$

$$q_e = k_F \cdot C_e^{1/m_F} \quad (5)$$

$$q_e = \frac{k_T \cdot q_T \cdot C_e}{[1 + (k_T \cdot C_e)^{m_T}]^{1/m_T}} \quad (6)$$

where q_e (μmol of adsorbate/g of adsorbent) is the amount adsorbed, C_e ($\mu\text{mol/g}$) is the monolayer capacity, k_L is related to the adsorption capacity, k_F is the equilibrium constant, $1/m_F$ is the adsorption intensity (also indicates the heterogeneity of the adsorbate sites), k_T is the Toth isotherm constant and m_T characterizes the heterogeneity of the system [24].

In addition, the adsorption process in porous adsorbents was also examined with a fractional approach to the equilibrium, used to estimate the effective diffusion coefficient $F(t)$ [3]:

$$F(t) = \frac{C_0 - C_t}{C_0 - C_e} = \sqrt{1 - \exp\left(-\frac{\pi^2 D t}{r^2}\right)} \quad (7)$$

where D (m^2/s) is the intraparticle-diffusion coefficient and r (m) is the particle size radius assuming a perfect sphere.

3. Results and discussion

3.1. Characterization of the adsorbents

The crystallographic phases present on the fresh LDH and on the calcined samples were analyzed by powder X-ray diffraction. The PXRD diffraction patterns obtained for the LDH structures dried at 353 K were shown in Fig. 1a. The results showed that single-phase materials were synthesized with the general formula $\text{Me}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ and the $3R_1$ polytype. The 2θ peaks located at 11.6° and 23.3° correspond to the diffractions of (003) and (006) basal planes of the LDH. Cell parameters were calculated using Bragg's equation with results represented in Table 1. *a* parameter was calculated as $a = 2d_{(110)}$ and represents the average distance between cations. The different metal ionic sizes of Me^{2+} in the host layer are responsible for the differences in the metal-metal distance as can be seen in Fig. 2. The *c*-parameter corresponds to three times the basal spacing and is related to the thickness of the

interlayer distance and was calculated as $c = 3/2 (d_{003} + 2d_{006})$. *c* values are also quite similar, as CO_3^{2-} was the interlayer anion in all cases with small changes having the opposite tendency to *a* values. Small differences between the samples could be related to changes in interstitial water content or anion orientation/ordering [25]. The crystallite size is related to the sharpness of the peaks and was calculated by the Scherrer equation from the (003) reflection. Zn_6Al_2 LDH pattern is best defined than the other three samples and has at least the double of crystallite size. The thickness of the crystallite follows the same trend as the ionic radius and the opposite one to the *c* parameter. Various authors have suggested that the number of layers of the LDH platelet in the order $\text{Zn} > \text{Co} > \text{Mg} > \text{Ni}$ could be responsible for the crystallite thickness [25, 26]. A higher crystallinity for Zn_6Al_2 hydrotalcites seems to be a general trend [25, 27–29]. Overall, (00l) reflections seem to have narrower and more symmetric peaks in comparison with (01l) ones. An overlap of the planes (009) and (012) can be seen in Co_6Al_2 , Ni_6Al_2 and especially in Mg_6Al_2 samples. The broadening of the (01l) reflections has been associated with stacking faults, in particular to the presence of $3R_2$ motifs introduced into our $3R_1$ polytype, rather than due to particle-size effects [30]. These stacking disorders are differentiated from turbostratic disorder which manifests in the line shape of the (*hk*0) reflections. Turbostratic disorder appears when successive layers are randomly orientated along the *c*-crystallographic axis, resulting in a loss of registry [31]. In our case Ni_6Al_2 sample, having a less defined (110) peak, could be the only sample affected. Samples were calcined for 4 h at 673 K (except for Mg_6Al_2 which was calcined at 823 K) causing the destruction of their layered structure and the formation of mixed oxides (see Fig. 1b). In the case of the Mg_6Al_2 sample the periclase crystal structure of magnesium oxide was formed and peaks appeared at 35° , 43° and 62° 2θ corresponding to the (111), (200) and (220) planes, respectively. In the Zn_6Al_2 sample zincite was formed with peaks appearing at 32° , 36° and 57° 2θ corresponding to the (100), (101) and (110) planes. Ni_6Al_2 sample transformed into nickel oxide with peaks at 37° (111), 43° (200) and 63° (220). Co_6Al_2 could have formed a Co_3O_4 structure with main peaks at 37° , 59° and 65° corresponding to (311), (333) and (440)

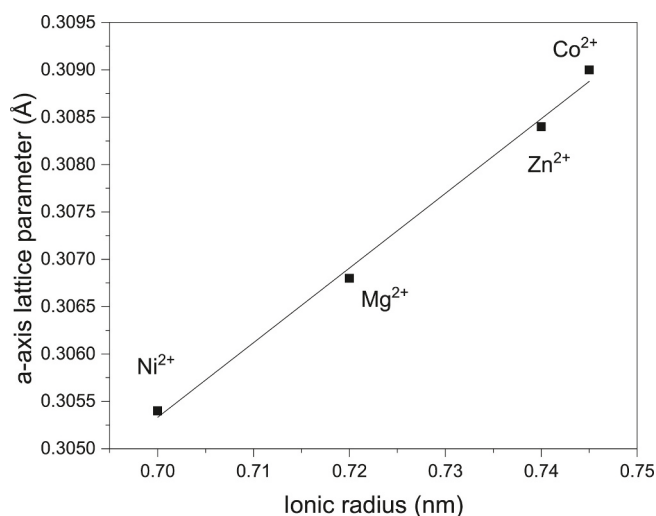


Fig. 2. Linear relationship between the dopant ionic radius and *a*-axis cell parameters.

respectively or a CoAl_2O_4 structure as their diffractogram peaks are at the same positions. XPS analysis will confirm the presence of Co_3O_4 spinel. The reconstruction of the LDH structure in the presence of water depends on multiple factors such as the temperature of calcination, the formation of spinels and the properties of the divalent metal ions present in the matrix. In our samples, Zn_6Al_2 and Mg_6Al_2 will recover its LDH structure in the presence of water whereas the memory effect does not appear for Ni_6Al_2 or Co_6Al_2 . The former would need to be heated up to 523 K and 4 MPa for 12 h [32] and, in the latter, because of the formation of the highly stable Co_3O_4 spinel even at low temperatures [33].

SEM analysis of the calcined samples was performed and the micrographs obtained are shown in Fig. 3. Higher resolution of Fig. 3c and especially Fig. 3a allows to distinguish the platelet-like structures, characteristic of hydrotalcite-like compounds, still present after calcination. EDX analysis shows a relatively small quantity of silicon (around 0.5%) present in all samples, which was also confirmed by XPS measurements, see below. Silicon comes from the aluminium extraction, as SiO_2 is usually present in the saline slags composition [8].

The adsorption-desorption isotherms of the samples both uncalcined (423 K) and calcined (673 or 823 K) are shown in Fig. S1. They all have a type II adsorption isotherm, related to the presence of nonporous or macroporous adsorbents, and a H3 hysteresis loop (IUPAC classification). This loop is caused by the typical non-rigid aggregates of plate-like particles with slit-shaped pores and does not exhibit a limiting adsorption at high relative pressures which implies a poor reliability in both the pore distribution and total pore volume [34]. The main textural properties of the samples dried at 423 K and calcined at 673 K (or 823 K) were summarized in Table 2. As it is frequent with LDH, in all samples the BET surface is greater when the samples are calcined: in the case of Zn_6Al_2 sample the difference is minimal (from 79 to 83 m^2/g) but in the other three samples it is close to double: from 113 to 200 m^2/g in Ni_6Al_2 , from 141 to 220 in Co_6Al_2 and from 115 to 245 in Mg_6Al_2 . This is due to the inaccessibility of nitrogen to the interlayer surface of the LDH due to both the relatively high charge density of the layers and the presence of CO_3^{2-} anions in the interlayer gallery [26]. The fact that zinc-containing samples have by far the smallest BET surface area could be related to its

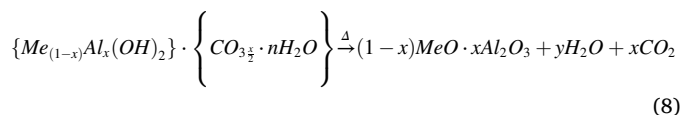
Table 2

Textural properties of the non-calcined and calcined LDH samples.

Sample		S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{HP} (cm^3/g)
Co_6Al_2	uncalcined	141	137	0.0006
	calcined	220	169	0.0273
Mg_6Al_2	uncalcined	115	103	0.0053
	calcined	245	218	0.0127
Ni_6Al_2	uncalcined	113	103	0.0042
	calcined	200	189	0.0042
Zn_6Al_2	uncalcined	79	71	0.0037
	calcined	83	73	0.0046

high crystallinity as its crystallite size twice bigger than those of all the other samples.

The thermal analysis behavior of the four LDH were examined with thermogravimetric analysis and differential thermal analysis. The results are represented in Fig. 4 and the different mass loss steps are calculated and summarized in Table 3. The LDH decomposed in five stages and with a total mass loss of between 30 and 45%. The first step, that goes up to 400 K, is related to the loss of adsorbed water and gases. The second, up to 500 K, corresponds to the loss of interlayer water. In the case of Ni_6Al_2 there is not a clear separation between the two steps. The third step is the biggest one in all the samples and is due to the loss of both CO_2 (decarbonation) and $-\text{OH}$ groups (dehydroxylation). In Ni_6Al_2 and Zn_6Al_2 two peaks can be observed. This step is located at different temperatures, Mg_6Al_2 is much more resistant to temperature changes than Co_6Al_2 , whose structure collapses relatively early. That is the reason why Mg_6Al_2 calcination temperature was chosen to be 823 K, to eliminate the carbonates in the interlayer. Steps 4 and 5 were small and correspond to the formation of the mixed metal oxide and the beginning of a sintering process which collapses the pores. The following equation [25] was used to calculate the theoretical decomposition products of the samples, considering that CO_3^{2-} exits the system as CO_2 .



The observed mass losses compared to those expected theoretically were included in Table 4. The different percentages of mass losses are mainly due to the atomic mass of the divalent metals. Large deviations were not found and Zn_6Al_2 had the best correlation between theoretical and empirical results which could be related to its higher crystallinity. In the case of Co_6Al_2 sample, if cobalt is present only as Co_3O_4 , the theoretical residue is larger than the measured residue, in accordance with the rest of the samples. This difference could be due to the water adsorbed outside the structure.

Temperature-programmed reduction by hydrogen (H_2 -TPR) was conducted to study the reducibility of the mixed oxides after calcination. Neither Zn_6Al_2 nor Mg_6Al_2 give significant peaks as can be seen in Fig. 5. Ni_6Al_2 sample exhibits one peak that goes from 600 to 1000 K with a maximum situated at 800 K which corresponds to the reduction of NiO to Ni . Co_6Al_2 profile shows two reduction steps: from 400 to 670 K, Co_3O_4 reduces to CoO and at 950 K changes from CoO to Co . This susceptibility to be reduced can have effects on its result in the butanol conversion, which will be later discussed.

X-ray photoelectron spectroscopy (XPS) was used for better understanding the surface characteristics of our calcined samples. The surface spectrum of the samples confirmed the EDX results, as a small percentage of Si is present in the samples. The relative proportion of the metals on the surface are shown in Table 5. The % of aluminum on the surface is a bit higher than the nominal ratio used 3:1. However this increase in Al concentration in the surface was to be expected as lighter metals tend to migrate to the surface with the increase of the temperature [35]. Spectra corresponding to Co 2p and Ni 2p were presented in Fig. S2. The calcination process of Co_6Al_2 oxidizes cobalt to form Co_3O_4

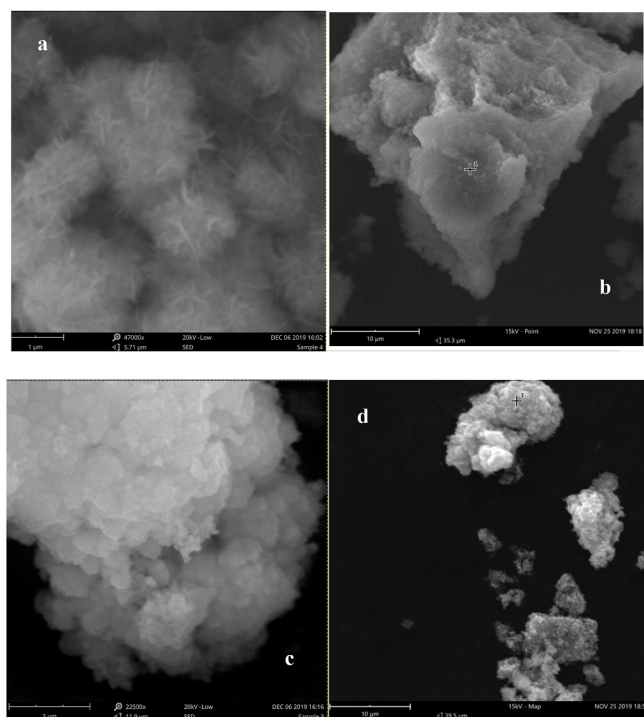


Fig. 3. SEM micrographs of the cobalt (a), magnesium (b), nickel (c) and zinc (d) samples.

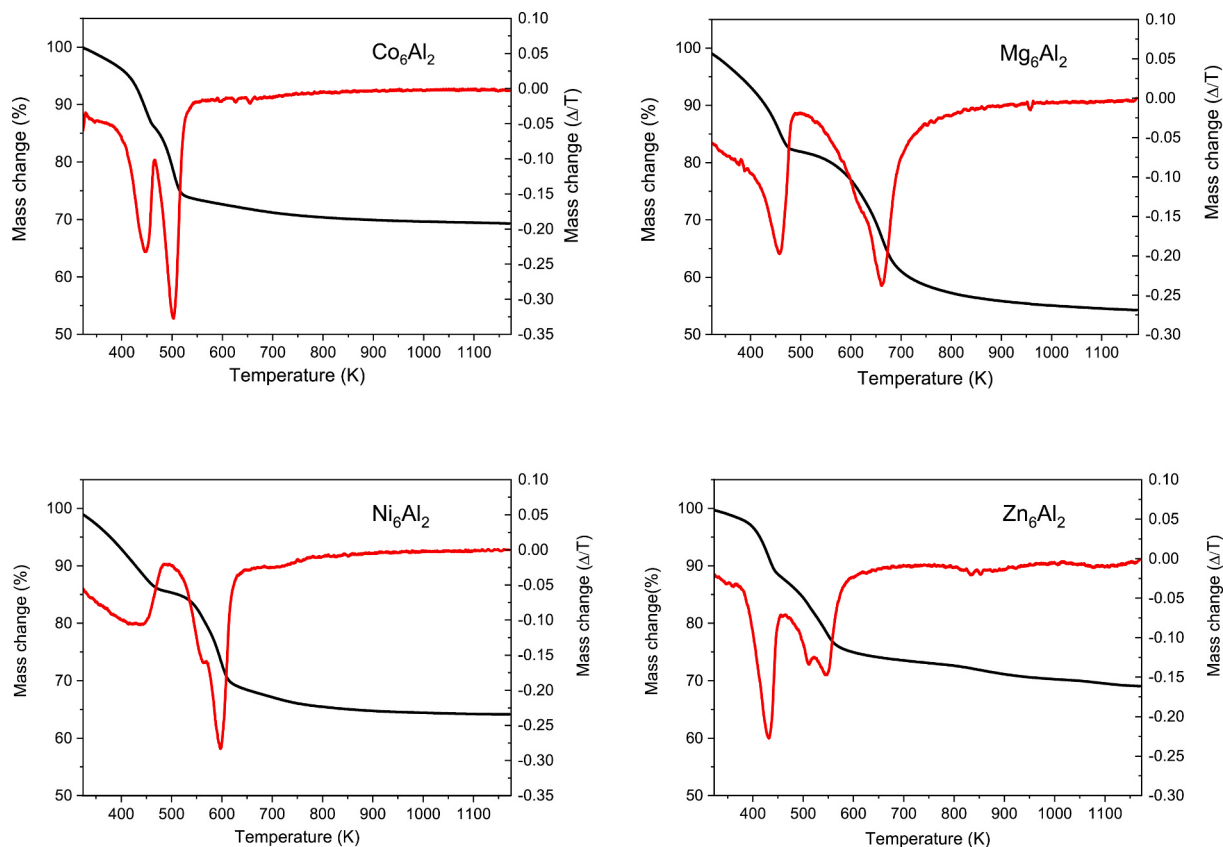


Fig. 4. TG and DTG curves of the LDH prepared with extracted aluminum.

Table 3

Mass losses (%) in the steps indicated from the thermogravimetric analyses of the LDH samples.

Step → Sample ↓	1	2	3	4	5	TOTAL
Co₆Al₂	300–400 K 3.95	400–465 K 10.00	465–538 K 12.35	538–823 K 3.4	823–1173 K 1.0	30.7
Mg₆Al₂	300–400 K 6.8	400–500 K 11.28	500–750 K 23.21	750–950 K 3.29	950–1173 K 1.12	45.7
Ni₆Al₂	300–500 K 14.69		500–650 K 16.94	650–850 K 3.34	850–1173 K 0.86	35.83
Zn₆Al₂	300–373 K 1.72	373–460 K 10.45	460–600 K 12.87	600–900 K 3.82	900–1173 K 2.08	30.94

Table 4

Comparison of theoretical remaining mass and measured remaining mass of the LDH samples.

LDH	Theoretical oxides structure	Theoretical remaining mass (%)	Measured remaining mass (%)	Variance from theoretical value
Co₆Al₂CO₃(OH)₁₆ · 4H₂O	2Co ₃ O ₄ + Al ₂ O ₃	71.89	69.30	–2.59
Mg₆Al₂CO₃(OH)₁₆ · 4H₂O	6MgO + Al ₂ O ₃	56.92	54.30	–2.62
Ni₆Al₂CO₃(OH)₁₆ · 4H₂O	6NiO + Al ₂ O ₃	67.89	64.17	–3.72
Zn₆Al₂CO₃(OH)₁₆ · 4H₂O	6ZnO + Al ₂ O ₃	69.40	69.06	–0.34

(Fig. S2a) as PXRD diffraction pattern suggested.

3.2. Acid and basic sites characterization

Metal oxides have been widely used for the dehydration/dehydrogenation of alcohols. Their different reaction pathways are employed as a model reaction that correlates with the strength and the concentration of the catalysts acid and basic sites [36]. 1-Butanol was used as reagent in this experiment. In general, acid sites tend to give predominantly dehydration products whereas basic sites dehydrogenate 1-butanol

[37–39]. As seen in Scheme 1, 1-butanol can be intramolecularly dehydrated into butene in the presence of acid sites. In a mainly acid catalyst, 1-butene will be rapidly isomerized and *cis/trans*-2-butene will be the main reaction products. An intermolecular dehydration can also occur with the formation of dibutylether. This mechanism should require the cooperation of both acid and basic sites to take place [37, 40]. It can also occur in mainly acid catalysts [41], however at temperatures above 550 K 1-butene is the main product [40]. In the same way, strong basic sites will prevent 1-butanol from being dehydrated and a dehydrogenation process will appear instead [40] (see Scheme 2).

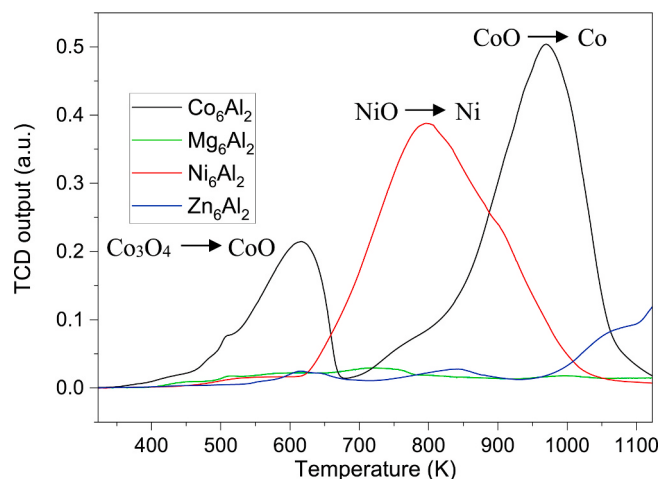


Fig. 5. H_2 -TPR profile of Co_6Al_2 , Mg_6Al_2 , Ni_6Al_2 and Zn_6Al_2 calcined samples.

1-Butanol is transformed then into butyraldehyde and both can react together to produce condensation products such as butyl-butyrate.

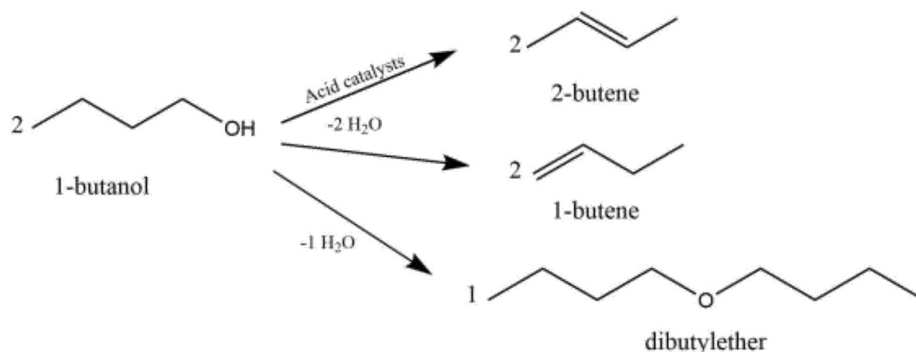
The active sites of mixed oxides obtained by the thermal decomposition of LDH are expected to vary upon modification of the Me^{2+} in the structure. The nature of their active sites has been studied before [42]: as a guiding principle our samples will have weak Brønsted basic sites related with surface $\text{HO}-$ groups; Lewis sites of medium-strength which are due to acid-basic pairs (both to $\text{Me}^{2+}-\text{O}^{2-}$ and $\text{Al}^{3+}-\text{O}^{2-}$); and strong Lewis basic sites which are associated with the presence of low coordinated O^{2-} . When trying to study the active sites' nature of our samples we have to deal with the fact that, in water adsorption experiments, we work mainly with meixnerite-like LDH (which are difficult to characterize because of their high degree of hydration) and, in the 1-butanol conversion, mixed oxides have been formed by LDH calcination. While some authors have found a precise correlation [43] between the basicity of the mixed oxides (Lewis-type) and that of meixnerite-like samples (Brønsted-type), others have reported a different behavior between Lewis and Brønsted sites [44].

The 1-butanol conversion with increasing temperatures is shown in Fig. S3a and Table 6. Co_6Al_2 , Ni_6Al_2 and Zn_6Al_2 have a similar behavior and reach 1-butanol conversion of around 85% at 623 K. However,

Table 5

Surface concentration (% atomic) and metals proportions of the calcined compounds on the surface of the LDH samples.

Sample	Me^{2+}	Al	O	C	Metals' proportions
Co_6Al_2	25.6	11	60.2	9.8	$\text{Co}_6\text{Al}_{3.5}$
Mg_6Al_2	26.2	8.3	51.9	13.5	$\text{Mg}_6\text{Al}_{1.9}$
Ni_6Al_2	21.4	10.7	53.1	14.8	Ni_6Al_3
Zn_6Al_2	20.4	8.8	49.5	21.2	$\text{Zn}_6\text{Al}_{2.6}$



Scheme 1. 1-butanol dehydration pathways.

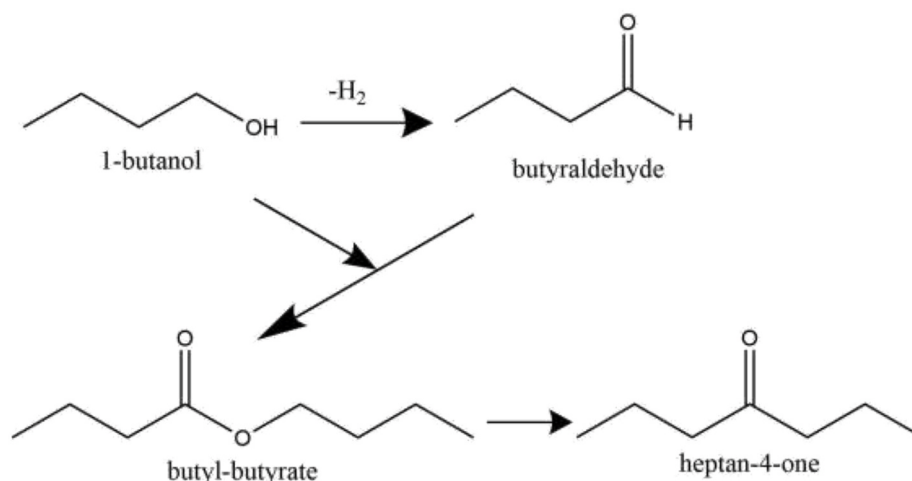
Mg_6Al_2 only manages to convert 38%. The results of the dehydration of 1-butanol (both to dibutyl ether and butene) show that it is the only sample that forms dibutyl ether (38%, Fig. S3b) and butene is formed by all the catalysts in various degrees (Fig. S3c). NH_3 -TPD experiments were performed on both Mg_6Al_2 and Zn_6Al_2 for a better understanding of the results (see Fig. 6). Both samples have medium strength acid sites assigned to Me^{2+} and Al^{3+} (peak at 550 K) and Mg_6Al_2 also has weak acid sites (peak at 475 K). These extra Brønsted acid sites together with the medium strength basic sites can favor the formation of dibutyl ether [45,46], since the two samples present a very similar density of acid centers ($5 \cdot 10^{-4} \text{ mmol/m}^2$). Cosimo et al. [47] found that ether formation is favored in the most hydroxylated samples (first peak in NH_3 -TPD). In addition, although MgO samples have few acid sites, the increasing presence of Al in the samples can be linearly related to their growth of acid sites number [47]. The dehydrogenation process favored by basic sites starts to the formation of butyraldehyde, samples selectivity towards it is shown in Fig. S3d. Ni_6Al_2 and Zn_6Al_2 have a similar selectivity percentage and Co_6Al_2 has a smaller one. This can be related with the catalysts susceptibility to be reduced. As seen in Fig. 5, in the range of temperatures considered (up to 623 K) Co_3O_4 is reduced to CoO in the presence of hydrogen and it should be expected that the most easily reducible catalysts would show highest selectivity towards higher degree of oxidation (butyl butyrate and heptanone), as seen in Figs. S3e and S3f [39]. The results found show that the LDH samples are characterized by the presence of basic surface sites. In the case of Mg_6Al_2 , the sample also presents acid sites since the formation of dibutylether requires the cooperation of acid and basic surface sites at this temperature.

3.3. Adsorption experiments

3.3.1. Effect of pH on adsorbate adsorption

Much care has to be taken when choosing the correct pH in adsorption tests. Diclofenac sodium is a salt of a weak acidic drug ($\text{pK}_a = 4.2$). At a pH of less than 3, it is mainly present in the free acid form which is less soluble than the salt and gives low signal in the UV-vis. As the pH increases both the ionized and unionized forms are present and the UV-vis signal grows and at a pH higher than 6 only the ionized form exists and the UV-vis signal is stable [48]. Salicylic acid ($\text{pK}_a = 2.8$) is in the protonated form, $\text{HOC}_6\text{H}_4\text{COOH}$, at a pH smaller than the pK_a and in the deprotonated form $\text{HOC}_6\text{H}_4\text{COO}^-$ at a pH bigger than 4.5. This deprotonation produces a small shift in the λ_{max} of the UV-vis spectrum [49].

The point of zero charge of the calcined hydrotalcites was 7.3 for Co_6Al_2 , 7.6 for Ni_6Al_2 , 8.3 for Zn_6Al_2 and 9.9 for Mg_6Al_2 as shown in Fig. S4. This rise in pH is due to the proton consumption that takes place when hydroxides are formed in the meixnerite structure. The differences between the samples can be related to the inability of Co_6Al_2 and Ni_6Al_2 to recover the LDH structure or/and the samples Me^{2+} average partial charge of oxygen which is also observed in the different decarbonation temperatures (see Table 3, step 3) as the carbonates will be more



Scheme 2. 1-butanol dehydrogenation pathways.

Table 6

Butane conversion percentages on the samples.

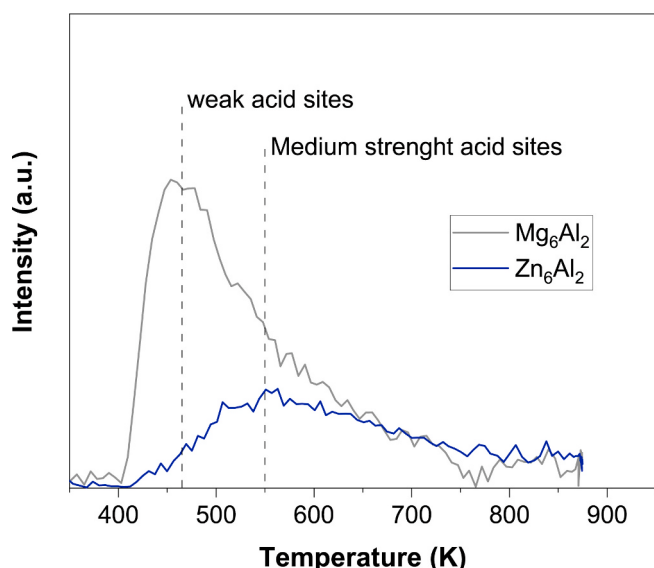
Sample	Conversion due mainly to acid sites (%)			Conversion due mainly to basic sites (%)			
	Butene	Dibutyl ether	Total	butyraldehyde	Butyl butyrate	Heptanone	Total
Co ₆ Al ₂	3.7	0.7	4.4	48.6	34.0	1.4	84
Mg ₆ Al ₂	5.4	46.4	51.8	29.9	7.8	0.1	37.8
Ni ₆ Al ₂	7.0	0.4	7.4	61.9	25.7	0.6	86.1
Zn ₆ Al ₂	13.2	0.5	13.7	65.0	19.2	0.4	84.6

attracted to more strongly charged oxygen [50]. When the pH is higher than the point of zero charge the overall surface charge of the adsorbents will be negative which causes an electrostatic repulsion between the adsorbate anions, decreasing the adsorption capacity. In addition, at a pH higher than 10.5, aluminum hydroxide dissolves and magnesium hydroxide precipitates [51]. Taking all this into account together with adsorption experiments performed at different pH (results not shown), a pH of 6 was chosen to perform all the adsorption tests.

3.4. Batch adsorption results

The results of the adsorption experiments for the four samples considering several adsorbent doses (100, 200 and 400 mg/L) and adsorbate concentrations (25, 50 and 75 $\mu\text{mol/L}$) are represented in Fig. 7 (diclofenac) and Fig. 8 (salicylic acid). The adsorbent dose effect is represented in the first columns of figures. As usual, an increase of adsorbent concentration implies a decline in the adsorption capacity. The change in drug concentration is represented in the second column; the increase of adsorbate concentration meant an increase of the adsorption capacity of the samples. At a 200 mg/L adsorbent concentration and 75 $\mu\text{mol/L}$ of adsorbate, the adsorption capacity of Zn₆Al₂ was the greatest, 301 $\mu\text{mol/g}$, followed by Mg₆Al₂ (159 $\mu\text{mol/g}$), Co₆Al₂ (59 $\mu\text{mol/g}$) and Ni₆Al₂ (36 $\mu\text{mol/g}$). These results are compared in Table 7 with those obtained in various studies using activated carbon from agro-industrial wastes. Activated carbon is usually taken as a reference because it has more stable properties than other adsorbents [52]. In the case of salicylic acid, in the same conditions, Mg₆Al₂ and Zn₆Al₂ show an equal 92 $\mu\text{mol/g}$ adsorption capacity, Ni₆Al₂ is not far at 83 $\mu\text{mol/g}$ and Co₆Al₂ adsorbs the least at 33 $\mu\text{mol/g}$. Although both salicylic acid and diclofenac are supposed to form a hydrogen bond between their COO⁻ group and the hydroxyl groups of the LDH, salicylic acid tends to form an intramolecular hydrogen bond with an adjacent hydroxyl group which causes a weaker affinity towards the adsorbent. The differences between the samples can be explained by the memory effect rather than the textural properties of solids. Zn₆Al₂ exhibits a much higher adsorption capacity than other materials despite its limited textural properties. Co₆Al₂ and Ni₆Al₂ are not capable of recovering its previous hydrothermal configuration which means that the interlayer adsorption is not produced causing a decline in their adsorption capacity.

Two types of kinetic modelling approaches have been proposed by several authors to describe the transport of adsorbates inside adsorbent surface and particles. One of this type of models considers simple relationships between the adsorption performance and operating

Fig. 6. NH₃ TPD patterns for Mg₆Al₂ and Zn₆Al₂ calcined samples.

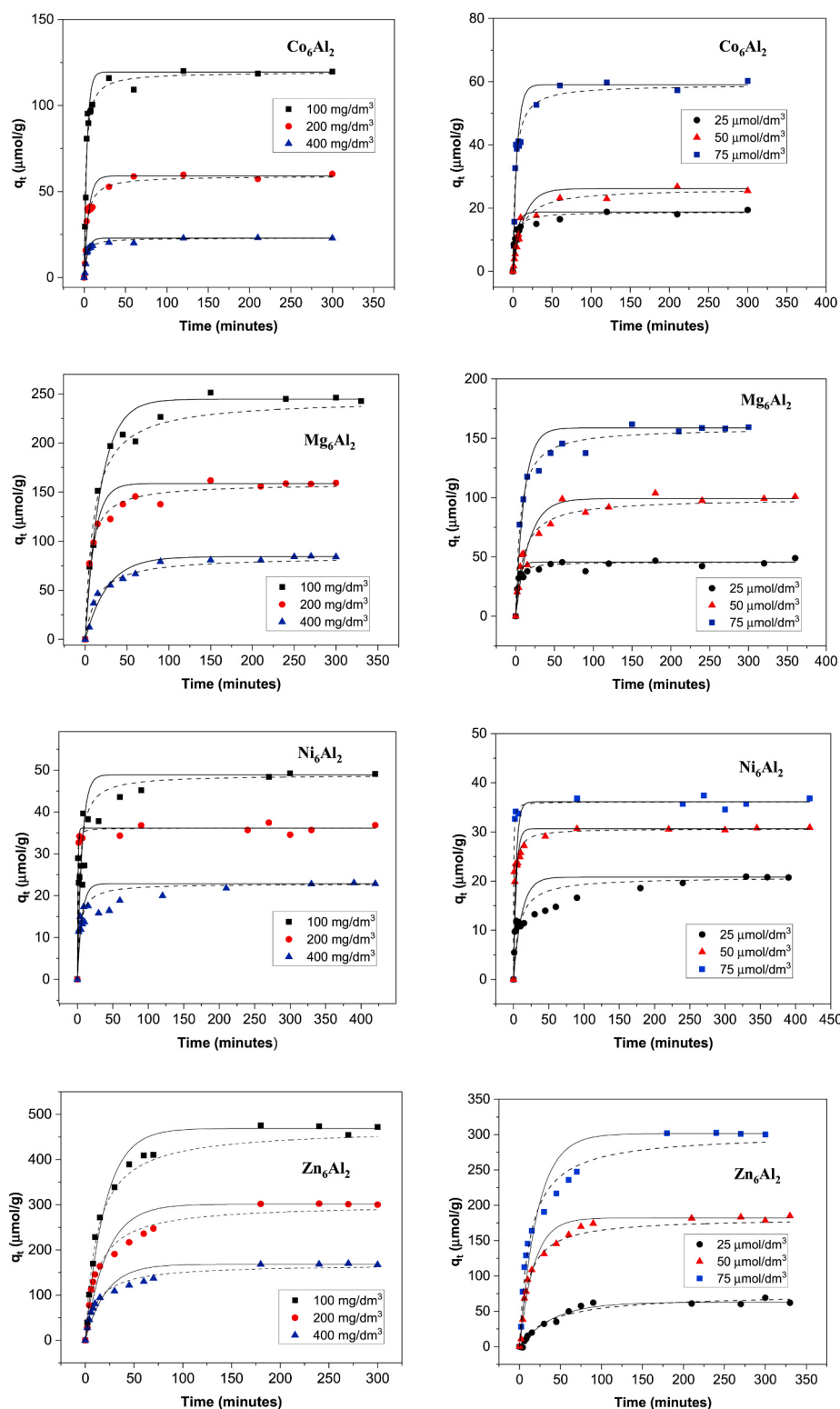


Fig. 7. Kinetic data for diclofenac adsorbed on Co_6Al_2 (first range), Ni_6Al_2 (second range), Mg_6Al_2 (third range) and Zn_6Al_2 (fourth range) with different amounts of adsorbent (first column) and different drug concentrations (second column). Adjustments to pseudo-first (solid line) and second order (dotted line) models are also shown.

conditions, showing how the mean adsorbent loading (q_t) changes with adsorption time (t). The second approach is the use of phenomenological models to describe the physics of the adsorption processes. The kinetic behavior of the samples was studied with pseudo-first and pseudo-second order linear reactions, simple models proposed from the first category of models, summarized in Figs. 7 and 8 and k_1 and k_2 values in

Tables S1 and S2. The goodness-of-fit of the samples was tested with chi square (χ^2) and the coefficient of determination (R). The results reveal that the adsorption procedure can be best described as a pseudo-second-order linear reaction. The k_2 values (see Table S2) are bigger for Co_6Al_2 and Ni_6Al_2 samples. The adsorption rate is bigger in those two samples and the equilibrium is also achieved faster (less than 100 min) than in

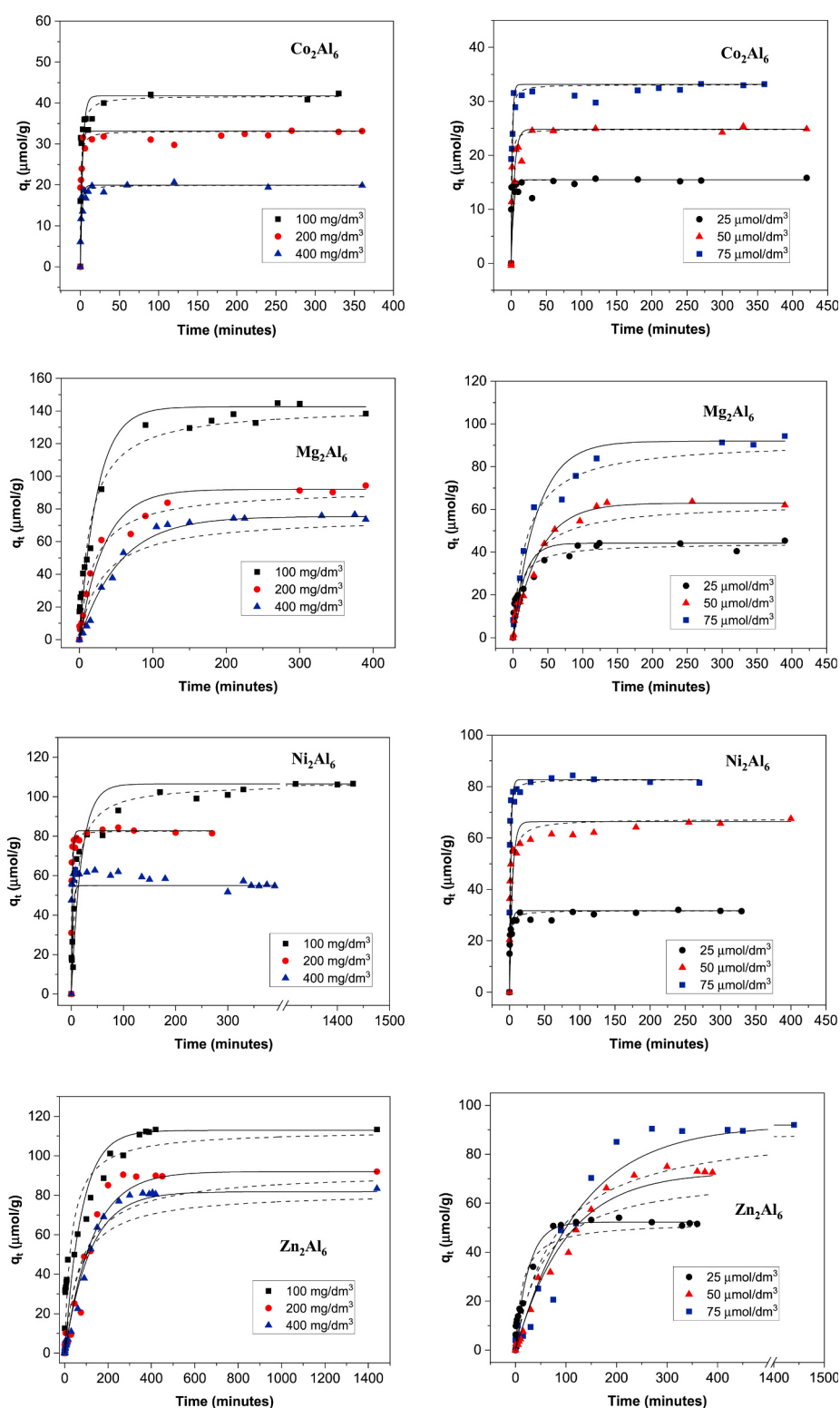


Fig. 8. Kinetic data of salicylic acid adsorbed on Co_6Al_2 (first range), Ni_6Al_2 (second range), Mg_6Al_2 (third range) and Zn_6Al_2 (fourth range) with different amounts of adsorbent (first column) and different drug concentrations (second column). Adjustments to pseudo-first (solid line) and second order (dotted line) models are also shown.

Table 7

Diclofenac adsorption capacities, comparison of several activated carbons obtained from different agro-industrial wastes.

Sample/precursor + activator	Adsorption conditions	C ₀ (mg/L)	Adsorption capacity (mg/g)	Ref.
AC from olive waste + H ₃ PO ₄	1.5 g/L, 298 K, pH 4.1	14.80	56.2	[54]
AC from olive stones + H ₂ SO ₄	5 g/L, 296 K, pH 4.2	25–150	11.01	[55]
AC from peach stones + H ₃ PO ₄	2.4 g/L, 298 K	30–530	200	[56]
AC from cyclamen tubes + ZnCl ₂	5 g/L, 298 K, pH 4	0–100	22.22	[57]
AC from pine chip + NaOH	1.6 g/L, 298 K, pH 7	5.923	372	[58]
Commercial AC + H ₂ SO ₄	25–100 mg/L, 298 K, pH 4.2–10	25–100	83–487	[59]
AC from cocoa pod husks	0.25–1.25 g/L, 298 K, pH 3–11	10–30	5.53	[60]
Co ₆ Al ₂ LDH, Al from saline slags	0.1–0.4 mg/L, 298 K, pH 6	8–24	6–38	This work
Mg ₆ Al ₂ LDH, Al from saline slags	0.1–0.4 mg/L, 298 K, pH 6	8–24	16–78	This work
Ni ₆ Al ₂ LDH, Al from saline slags	0.1–0.4 mg/L, 298 K, pH 6	8–24	7–16	This work
Zn ₆ Al ₂ LDH, Al from saline slags	0.1–0.4 mg/L, 298 K, pH 6	8–24	20–150	This work

Table 8

Freundlich, Langmuir and Toth parameters for the adsorption of diclofenac by the LDH. Equilibrium time = 24 h, T = 298 K, pH = 6.

	Mg ₆ Al ₂	Zn ₆ Al ₂
Freundlich		
q _F	97	91
m _F	2.5	2.2
χ ²	1047	1756
R	0.95	0.95
Langmuir		
q _L (μmol/g)	1006	1363
k _L (mL/μmol)	0.024	0.020
χ ²	545	167
R	0.98	0.97
Toth		
q _T (μmol/g)	1980	2013
K _T (mL/μmol)	0.043	0.025
m _T	0.39	0.54
χ ²	19,790	8070
R	0.995	0.999

Mg₆Al₂ and Zn₆Al₂ samples. This could be due to: a) the time taken by both LDH to recover their structure when put in contact with water and/or b) the time taken by the drugs to enter the interlayer in those two samples. An analysis of the *k*₂ values also shows that it decreases as the initial organic molecule concentration increases from 25 to 75 μM and as the adsorbent mass decreases from 400 to 100 mg/L. These results could be related to the number of active sites available for adsorption. The effective diffusion coefficient calculations are presented in Table S3. There is no clear tendency in the samples as adsorbent mass and adsorbate concentration are increased. However, sample comparison makes clear that *D*/*r*² is significantly bigger in Co₆Al₂ and Ni₆Al₂ than the other two samples, as expected from the adsorption kinetics. Constants calculated from the isotherm equations are displayed in Table 8. All models show a good representation of the experimental results (see Fig. S5), although the Toth equation shows a better accordance between the theoretical and experimental results than Langmuir and Freundlich equations. Toth model has already been proven to give a good correlation of adsorption experiments with activated carbons and organic molecules [53].

There may be a relationship between the acid/basic properties of the LDH samples and the adsorption capacity of the contaminants. In this case, it is possible to observe a relationship between the amount of adsorbed pollutants (per external area) and the acidic properties of the adsorbents, see Fig. 9. The figure represents the maximum amount adsorbed of the two pollutants and per external area of adsorbent (see Table 2) in order to avoid the limitation of the diffusion of pollutants inside of the structure of the LDH samples. As acidic properties, the selectivity to butenes observed in the dehydration reaction of 1-butanol has been considered. In the case of the basic properties, a similar relationship could be obtained, but the samples with the presence of Co and Ni show a greater performance in dehydrogenation, related to the

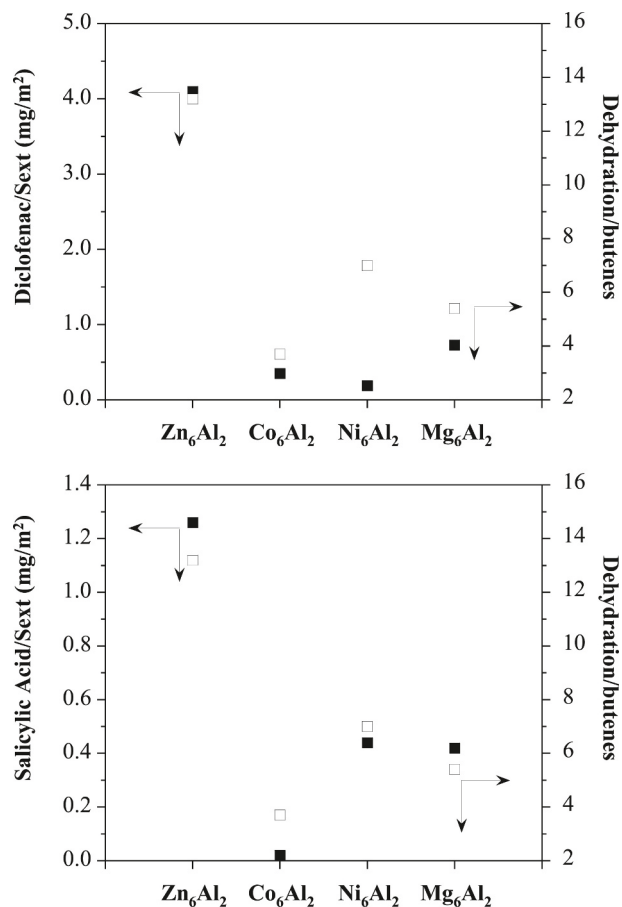


Fig. 9. Evolution of the amount of pollutants adsorbed/Seft to the butenes formation in the dehydrogenation reaction of 1-butanol. (■) pollutants, (□) dehydrogenation.

properties of these metals, as already mentioned above from the TPR analysis performed.

4. Conclusions

A series of LDH with various Me²⁺ and a ratio of 3:1 was synthesized using Al³⁺ extracted from saline slags as aluminum source. All the samples have a LDH structure with differences between samples mainly due to Me²⁺ cations. Adsorption experiments of diclofenac and salicylic acid as examples of emerging contaminants were performed. Zn₆Al₂ and Mg₆Al₂ present the best adsorption capacity mainly due to their ability to recover their LDH structure when rehydrated. The adsorption capacities of the adsorbents correspond quite well to their acidic properties. Not so much in the case of the basic properties because the

dehydrogenating capacity of the LDH samples is also affected by the redox properties of metals, Ni and Co.

CRediT authorship contribution statement

L. Santamaría: Formal analysis, Writing - original draft. **F. Devred:** Formal analysis. **E.M. Gaigneaux:** Formal analysis. **M.A. Vicente:** Formal analysis, Writing - original draft. **S.A. Korili:** Formal analysis, Writing - original draft. **A. Gil:** Conceptualization, Project administration, Writing - original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2020.110560>.

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