



**HAL**  
open science

## Layered double hydroxides and LDH-derived materials in chosen environmental applications: a review

Dylan Chaillot, Simona Bennici, Jocelyne Brendlé

► **To cite this version:**

Dylan Chaillot, Simona Bennici, Jocelyne Brendlé. Layered double hydroxides and LDH-derived materials in chosen environmental applications: a review. *Environmental Science and Pollution Research*, In press, 10.1007/s11356-020-08498-6 . hal-02958114

**HAL Id: hal-02958114**

**<https://hal.science/hal-02958114v1>**

Submitted on 5 Oct 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Layered Double Hydroxides and LDH-derived materials in chosen environmental applications: a review

*Dylan Chaillot<sup>1,2</sup>, Simona Bennici<sup>1,2,\*</sup>, Jocelyne Brendlé<sup>1,2</sup>*

<sup>1</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>2</sup> Université de Strasbourg, France

\*Corresponding author: [simona.bennici@uha.fr](mailto:simona.bennici@uha.fr)

**Keywords:** Hydrotalcite, layered double hydroxides, materials, synthesis, applications, industrial, environmental.

## Abstract

With increasing global warming awareness, layered double hydroxides (LDHs), hydrotalcites and their related materials are key components to reduce the environmental impact of human activities. Such materials can be synthesized quickly with high efficiency by using different synthesis processes. Moreover, their properties tunability is appreciated in various industrial processes. Regarding their physical and structural properties, such materials can be applied in environmental applications such as the adsorption of atmospheric and aqueous pollutants, the hydrogen production, or the formation of 5-Hydroxymethylfurfural (5-HMF). After a first part dedicated to the synthesis processes of hydrotalcites, the present review reports on specific environmental applications chosen as example in various fields (green chemistry and depollution) that have gained increasing interest in the last decades, enlightening the links between structural properties, synthesis route and application using the lamellar materials.

25 **Introduction**

26 Layered double hydroxides, also called LDHs or anionic clays, are particular lamellar  
27 materials made of octahedral sheets composed of metallic cations in the center of the  
28 octahedra. These materials can be found in nature, and present the brucite (Mg(OH)<sub>2</sub>)  
29 structure with divalent cations M<sup>II</sup> (Mg<sup>2+</sup> or Cu<sup>2+</sup> for example) partly substituted by trivalent  
30 cations M<sup>III</sup> (such as Al<sup>3+</sup> or Fe<sup>3+</sup>). This partial substitution induces a positive charge deficit  
31 that is compensated by anions, such as carbonates, located in the interlayer space along with  
32 water molecules. The easily accessible interlayer is one of the sources of the anion exchange  
33 capacity of the compounds, and of its ability to capture and exchange anions. This  
34 characteristic is almost unique for inorganic materials, indeed clay minerals exhibit cation  
35 exchange capacity. Thanks to these characteristics, they are appreciated for their versatility,  
36 simplicity of tailoring and low cost. The general formula of LDHs can be described as  
37 follows:



39 where M<sup>II</sup> and M<sup>III</sup> respectively represent the metallic divalent (Mg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) and  
40 trivalent (Al<sup>3+</sup>, Fe<sup>3+</sup>) cations, A the compensating anion, and x and m depend on the  
41 substitution rate between M<sup>II</sup> and M<sup>III</sup> cations.

42 Hydrotalcites are particular LDHs (characterized by a Mg:Al molar ratio of 3:1) in which  
43 magnesium is partly substituted by aluminum. Specific properties such as porosity and  
44 surface area can be tailored by varying the synthesis method and conditions, leading to a wide  
45 range of materials adapted to targeted applications. The structure can also be modified by  
46 changing the combination of the cations and the interlayer anions, in order to confer specific  
47 properties, (Homsı et al. 2017; El Roubı et al. 2018; Sheng et al. 2019; Wu et al. 2019a).

48 LDHs can be synthesized by various techniques depending on the final requirements such  
49 as high crystallinity, low time and/or energy consuming reaction, and phase purity. The most  
50 common methods used to synthesize these materials are hydrolysis reaction, co-precipitation,

51 hydrothermal synthesis, steam activation, microwave irradiation, and sol-gel. These fast and  
52 environmental-friendly synthesis processes, combined to high sorption capacities, allow the  
53 use of hydrotalcites and derived materials in various applications, such as adsorption of  
54 various molecules (organic and inorganic pollutants or dyes for example) or catalytic  
55 processes (also thanks to the presence of strong basic sites). In particular, these materials have  
56 been intensively studied as catalysts and catalyst supports based on their specific  
57 physicochemical features.

58 Mixed oxides, obtained from the calcination of the parent material, are most generally used  
59 in catalytic and environmental applications, due to the high temperatures required. The  
60 composition of the obtained oxides depend on the initial combination of  $M^{II}$  and  $M^{III}$  cations  
61 (El Rouby et al. 2018; Rahmanian et al. 2018; Sheng et al. 2019; Wu et al. 2019a), but also on  
62 the heating temperature and the targeted reaction (dehydration, dehydroxylation, removal of  
63 the interlayer anion, and oxide reformation). Considering the rising interest in using  
64 synthesized LDHs for various applications, this paper reviews the most common synthesis  
65 methods for their preparation and some chosen environmental applications (Fig1). Due to the  
66 wide panel of applications involving layered double hydroxides and LDH-derived materials,  
67 the list of applications here reported is not exhaustive. Moreover, certain applications have  
68 been already extensively reported in the literature and they could represent alone the subject  
69 of dedicated review articles (for example in the case of biodiesel production (Helwani et al.  
70 2009; Atadashi et al. 2013)).

71	Abstract .....	1
72	Introduction .....	2
73	1. Synthesis techniques for hydrotalcite-like compounds.....	4
74	1.1. Co-precipitation method .....	4
75	1.2. Urea hydrolysis .....	7
76	1.3. Sol-gel method.....	9
77	1.4. Hydrothermal treatment.....	10

78	2. Use of hydrotalcites and derived materials in environmental applications .....	13
79	2.1. Adsorption of atmospheric pollutants.....	14
80	2.1.1. CO <sub>2</sub> adsorption – Capture and storage .....	14
81	2.1.2. NO <sub>x</sub> and SO <sub>x</sub> adsorption .....	21
82	2.1.3. VOCs total decomposition .....	27
83	2.1. Adsorption of aqueous pollutants .....	30
84	2.2. Other applications.....	36
85	2.2.1. Hydrogen production.....	36
86	2.2.2. 5-Hydroxymethylfurfural formation .....	39
87	Conclusion.....	42
88	References .....	43

## 89 1. Synthesis techniques for hydrotalcite-like compounds

90 As previously explained, hydrotalcite (and more generally LDHs) can be **of natural origin**  
91 **(alteration minerals)** or **synthetic**. The advantages in synthesizing LDHs are the ability to  
92 finely tune the **mineral properties in the view of a specific application**, by finding the  
93 appropriate combination of reactants and **the adapted M<sup>II</sup>/M<sup>III</sup>** molar ratio. The most important  
94 factors to **be considered are** the nature of the metallic cations, the pH, the temperature, the  
95 ageing time, and the preparation method. Several synthesis methods have been developed  
96 during the last decades, but this review **summarizes only those** most commonly used and  
97 described in **the** literature.

98

### 99 1.1. Co-precipitation method

100 **Co-precipitation** is the most common **method** to synthesize LDHs. It consists in dissolving  
101 **the** inorganic salts in alkaline media, at constant or increasing pH. This reaction allows to  
102 control the morphology and particle size, depending on the supersaturation of the solution.  
103 Feitknecht reported for the first time in 1942 on the LDH synthesis by co-precipitation. [Mg-  
104 Al-CO<sub>3</sub>] LDH was synthesized starting from diluted solutions of the reactants. The **co-**  
105 **precipitation** synthesis process has been then studied years later by Gastuche et al. (1967) and

106 Miyata (1975, 1980) by modifying parameters such as the concentrations of the reactants and  
107 the washing conditions. They also introduced the control of the pH as a key parameter for the  
108 formation of LDHs. Several studies have been performed later, focusing on the substitution of  
109 the type of metallic cations in the structure of the LDHs, as shown by Sato et al. (1988), in  
110 order to obtain several LDH with different structural formulas ( $M^{II} = Mg^{2+}$ ,  $Ni^{2+}$  or  $Co^{2+}$  and  
111  $M^{III} = Al^{3+}$  or  $Fe^{3+}$ ). **Co-precipitation** allows to finely tune the structure of the **synthesized**  
112 materials by controlling the  $M^{II}/M^{III}$  molar ratios, the type of interlayer anion, the synthesis  
113 **duration**, the temperature, **and** the pH of the solution (Thevenot et al. 1989; Ulibarri 2001;  
114 Zhao et al. 2003; Klopogge et al. 2004; Sharma et al. 2007; Klemkaite et al. 2011).

115 **Co-precipitation** can be performed at low or high supersaturation **conditions** depending on  
116 the desired crystallization state, as long as the initial concentration of the reactants is above  
117 the saturation state of the solution (supersaturation conditions). In any case, the pH of the  
118 solution must be controlled: a pH value too low does not allow the complete precipitation of  
119 all metallic ions, while a too high value leads to the leaching of one or more metallic ions.  
120 Basic media are **preferred** in most cases, but the optimal pH depends mainly on the metal  
121 cations used. Fig2. **presents** the steps involved in the co-precipitation synthesis process. The  
122 **co-precipitation** method **performed** at low supersaturation **conditions** has been firstly  
123 documented in the '90s by Kannan et al. (1995). This technique is performed by the slow  
124 addition of solutions containing the divalent and trivalent cations in **the** appropriate molar  
125 ratio, before adding an aqueous solution of the chosen interlayer anion (Kannan et al. 2004;  
126 Climent 2004; Klopogge et al. 2004; Kovanda et al. 2005a; Perez-Lopez et al. 2006; Sharma  
127 et al. 2007; Wang et al. 2011; Klemkaite et al. 2011; Balsamo et al. 2012). An alkaline  
128 solution is then added in order to fix the pH during the reaction and to promote the **co-**  
129 **precipitation** of the two metal salts. This synthesis process has been well described by a  
130 schematic flow chart edited by El Rouby et al. (2018). The advantage of this method is the

131 possibility to control the charge density by keeping the pH constant under low supersaturation  
132 conditions by the addition of a mixture of NaOH and NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> (Sharma et al.  
133 2007; Wang et al. 2011; Klemkaite et al. 2011; Balsamo et al. 2012; Sheng et al. 2019; Li et  
134 al. 2019a). Materials obtained by co-precipitation at low supersaturation present a higher  
135 crystallinity than those obtained at high supersaturation conditions thanks to the continuous  
136 regulation of the pH of the synthesis solution. In the high supersaturation condition, the  
137 concentration of the solutions is continuously increased or the solution containing the  
138 dissolved salts is added to a solution containing a small excess of alkali bicarbonates. This  
139 process leads to the formation of less crystalline materials than low supersaturation method,  
140 but gives rise to a high number of small aggregates due to the interlayer confinement effect of  
141 the carbonate ions (Zhang et al. 2008; Abelló et al. 2010; Solovov et al. 2018).

142 Co-precipitation synthesis can be considered as an efficient method to obtain crystalline  
143 materials, particularly thanks to the long synthesis duration time (several days), the controlled  
144 synthesis pH, and the addition of post treatments such as hydrothermal treatment for example  
145 (Kannan et al. 1995; Kloprogge et al. 2004). However, due to the large dimension of the  
146 obtained particles the specific surface area values (between 50-100 m<sup>2</sup>.g<sup>-1</sup>) are lower than  
147 those obtained by sol-gel synthesis (150-200 m<sup>2</sup>.g<sup>-1</sup>), and discussed later in this review  
148 (Aramendía 2002; Park et al. 2018). The substitution with other metallic cations, such as Fe,  
149 Zn, Cu, and Ni, as demonstrated by Gevers et al. (2019), add the possibility to modify the  
150 crystallite dimensions and influence the thermal stability of LDHs. Thermal treatments, such  
151 as hydrothermal treatment or microwave irradiation, can be performed to improve  
152 crystallinity and/or to reduce the synthesis time. Similar structures are then obtain even with  
153 shorter synthesis time (Climent 2004). This progress was reported by Tichit et al. (2002) by  
154 comparing microwave and hydrothermal treatments in co-precipitated hydrotalcites. The  
155 authors did not find any significant differences in the structural properties of the final

156 material, despite the shorter synthesis time that represent a clear advantage. The thermal  
157 treatment **presents** a significant impact on the structural properties of the materials: Othman et  
158 al. (2006) compared the effect of the hydrothermal treatment on hydrotalcites prepared by **co-**  
159 **precipitation** and sol-gel methods. They showed that the specific surface area and pore sizes  
160 **significantly** increased in both cases, with a **stronger impact on** the samples synthesized by  
161 sol-gel.

162

## 163 **1.2. Urea hydrolysis**

164 Urea is a weak Brönsted base highly soluble in water. It can be used as **a** precipitating agent  
165 instead of sodium hydroxide to **increase** the pH through its **thermal decomposition**. The slow  
166 decomposition, starting around 90°C, leads to an increase of the pH up to 10 (Costantino et al.  
167 1998; Yang et al. 2004). Since urea decomposes slowly, it leads to a lower degree of  
168 supersaturation. Moreover, prolonged hydrolysis results in the formation of  $\text{CO}_3^{2-}$  anions in  
169 basic medium that act as interlayer anions. **Therefore**, urea enables an efficient pH control and  
170 the formation of mono-dispersed LDH materials with high crystallinity through a low-cost  
171 method (Adachi-Pagano et al. 2003; Yang et al. 2004; Zeng et al. 2009a; Xu et al. 2016; Park  
172 et al. 2018). The purity and crystallinity of hydrotalcite phases can also be optimized **by**  
173 **tuning the**  $\text{M}^{\text{II}}:\text{M}^{\text{III}}$  molar ratio, **the** urea concentration, and **the** ageing time (Costantino et al.  
174 1998; Zeng et al. 2009a; Berber et al. 2013; Montañez et al. 2014; Zhang et al. 2014; Bian et  
175 al. 2016; Xu et al. 2016; Park et al. 2018). **As an exemple**, Berber et al. (2013) **identified** the  
176 optimal synthesis conditions **to** obtain uniform and highly crystalline hydrotalcite particles by  
177 using a urea/metallic cation molar ratio of 2, and 12h of ageing time at 120°C. Secondary  
178 phases have been observed with molar ratios lower or greater than 2, leading to lower  
179 crystallinity and specific surface areas of the materials. The main steps **involved in**  
180 hydrotalcite synthesis via urea hydrolysis **are summarized** in Fig3.



181 Most of the time, this technique is combined to others (in which urea is used only as a  
182 precipitating agent), such as co-precipitation or hydrothermal synthesis. The combination of  
183 urea hydrolysis and hydrothermal treatment has been well-documented by Berber et al. (2013)  
184 and Benito et al. (2006) in order to obtain uniform particles, but also by Rao et al. (2005) to  
185 find optimal Mg:Al molar ratios of 1:1 and 2:1 with uniform and small particles' size. In the  
186 first article, microwave irradiation was used as heating source in the synthesis process,  
187 strongly shortening the synthesis time and the formation of pure and well-crystallized  
188 hydrotalcite phases presenting high specific surface areas. Further studies were performed by  
189 Montañez et al. (2014) by comparing the properties of mixed oxides obtained by calcination  
190 of a series of Ni-Al-Mg hydrotalcites synthesized, either by co-precipitation or by urea  
191 hydrolysis. Enhanced redox properties, larger pore sizes and smaller particles (interesting  
192 features in catalytic applications) were obtained on calcined samples prepared with urea  
193 hydrolysis. In general, the use of microwave irradiation allows to reduce the preparation time  
194 without to impact on the structural and physical properties. This methodology is of a great  
195 interest for the industrial scaling-up (Yang et al. 2007; Benito et al. 2008). Hibino and Ohya.  
196 (2009) combined urea hydrolysis with hydrothermal treatment in order to remove certain by-  
197 products (i.e. hydrated magnesium carbonate hydroxide phases). Further studies have been  
198 performed by Kloprogge et al. (2006) to show the evolution of the intercalated species  
199 depending on the hydrothermal treatment:  $(\text{NH}_2)\text{COO}^-$  tends to directly form after  
200 precipitation, but slowly transforms into carbonated species during the hydrothermal  
201 treatment.

202 As a partial conclusion, urea hydrolysis is a slow reaction that leads to a low degree of  
203 supersaturation during the precipitation. It presents the advantage to provide large and thin  
204 platelets with a narrow particle size distribution in a shorter ageing time than co-precipitation  
205 (Naseem et al. 2019). However, the decomposition of urea leads to the formation of  $\text{CO}_2$  that

206 reacts with water to form carbonates and acting as compensating anions (Thomas 2012). In  
207 this case, a further anion exchange may be required depending on the targeted application  
208 (Bish 1980; Iyi et al. 2004; Inayat et al. 2011).

209

### 210 1.3. Sol-gel method

211 The sol-gel method is appreciated for its low cost, low energy and limited time consuming,  
212 for the possibility to obtain high purity materials, and for the possibility to tune their  
213 composition (Lopez et al. 1996; Paredes et al. 2006; Sharma et al. 2007; Ramos-Ramírez et al.  
214 2009; Lee et al. 2016). This process allows to control the structural properties of the final  
215 materials by simply varying the chemical nature of the reactants, the ageing time, and by  
216 removing/adding reactant species. This technique consists in dissolving the desired metal  
217 sources (inorganic salts or metal organic compounds) in water, at room temperature (Fig4.).

218 The concentration of the metal cations can be varied to tune the substitution ratio of  $M^{II}$  and  
219  $M^{III}$  cations and to obtain a wide range of materials (Corma et al. 1994; Valente et al. 2007,  
220 2009; Sharma et al. 2007). The appropriate amount of acid or base is then added to the  
221 reactants' solution during hydrolysis to favor the condensation reaction. The solution is finally  
222 aged during several hours or days, at room temperature or lightly heated up to 100°C. Prince  
223 et al. (2009) proposed a general sol-gel method for the preparation of LDHs that can be  
224 adapted to obtain materials containing specific metallic cations and possessing a defined  
225 morphology in the view of a specific application. Ramos-Ramírez et al. (2009) also evidenced  
226 the formation of small amounts of brucite phase, in addition to hydrotalcite, with a Mg/Al  
227 molar ratio of 2 and explained this behavior by the similar structure of the two materials.  
228 Synthetic hydrotalcites can also be calcined and rehydrated without losing their lamellar  
229 structure. During regeneration, they show a “memory effect”, as evidenced by Climent et al.  
230 (2004) by using rehydrated sol-gel hydrotalcites for pharmaceutical applications.

231 Several parameters can be varied to improve the crystallinity (Kovanda et al. 2005b;  
232 Valente et al. 2009) of the particles, to modify their morphology (Valente et al. 2007, 2009,  
233 2010), and to enhance the surface area (Corma et al. 1994; Lopez et al. 1996, 1997a; Climent  
234 et al. 2004; Paredes et al. 2006; Valente et al. 2007; Prince et al. 2009). Parameters, as the  
235 composition of the aqueous media, the pH, and the ageing time, were considered (Corma et al.  
236 1994; Kovanda et al. 2005b). Lopez et al. (1997b) studied the impact of different alkoxides,  
237 such as magnesium ( $\text{Mg}(\text{OEt})_2$ ) and aluminum ( $\text{Al}(\text{NO}_3)_3$ ), used as reactants, on the thermal  
238 stability of a series of hydrotalcites. Most of the time, the comparison between the synthesis  
239 techniques and the parameters evidences the interest of using one or the other specific  
240 method, generally sol-gel or co-precipitation (Jitianu et al. 2000; Prinetto et al. 2000;  
241 Bolognini et al. 2003; Othman et al. 2006; Valente et al. 2007, 2010; Smalenskaite et al.  
242 2017). Smalenskaite et al. (2017) compared sol-gel and co-precipitation for the preparation of  
243 cerium-substituted Mg-Al LDHs; Othman et al.(2006) studied the impact of the thermal  
244 treatment on the structure of similar materials. In many cases, the sol-gel approach is  
245 preferred for its simplicity and the high quality of the materials obtained (Ramos et al. 1997;  
246 Othman et al. 2006; Valente et al. 2010; Lee et al. 2016; Smalenskaite et al. 2017).

247 The sol-gel synthesis method is appreciated for its high reproducibility, the high  
248 homogeneity and purity of the obtained compounds, the small size of the particles (nanoscale)  
249 and their high specific surface area (Prince et al. 2009; Smalenskaite et al. 2017; Valeikiene et  
250 al. 2019). However, lower crystallinity is generally observed through this synthesis route  
251 (Smalenskaite et al. 2017). Often and depending on the final application of the materials,  
252 additional steps such as sonication, microwave irradiation (Benito et al. 2006) or  
253 hydrothermal treatment are required.

254

#### 255 **1.4. Hydrothermal treatment**

256 As **previously reported**, the synthesis of LDHs by **co-precipitation**, sol-gel method or urea  
257 hydrolysis can be optimized by hydrothermal treatment in order to improve the crystallinity  
258 and the size of the crystallites (Kloprogge et al. 2004; Sharma et al. 2007). The treatment  
259 generally occurs under mild hydrothermal conditions, up to 200°C, autogenous pressure, **with**  
260 **durations between** hours to several days. Fig5. **displays** the hydrothermal synthesis process.

261 Besides the improvement of the crystallinity, hydrothermal synthesis can be directly used as  
262 a synthesis method, in order to form LDH phases with increased particle sizes. It consists in  
263 dissolving the metallic salts into a solvent (generally water) before putting the solution into a  
264 stainless-steel reactor and heating under hydrothermal conditions, generally under medium  
265 temperatures (30-300°C) and steam pressure, with different synthesis times (few hours to  
266 several days) (Xu and Lu 2005; Liao et al. 2012; Bontchev et al. 2003; Bankauskaite and  
267 Baltakys 2011; Lin et al. 2019; Budhysutanto et al. 2010; Roelofs et al. 2001; Jang et al.  
268 2014). Several reactants such as inorganic salts and minerals can be used as metal sources.  
269 **Most commonly**, metal oxides and hydroxides (Xu and Lu 2005; Budhysutanto et al. 2010;  
270 Jang et al. 2014; Labuschagné et al. 2018) or nitrate salts (Roelofs et al. 2001; Bontchev et al.  
271 2003; Lin et al. 2019) are used as reactants, but other sources can be used: Ogawa et Asai  
272 (2000) **used for example natural minerals** (brucite and gibbsite) as starting materials to  
273 intercalate organic guests. Liao et al. (2012) also used natural brucite and Al(OH)<sub>3</sub> as  
274 synthesis reactants to study the morphology and structural properties of hydrotalcites obtained  
275 under different synthesis conditions.

276 Like **for** the other synthesis techniques, the Mg:Al molar ratio and the interlayer anions can  
277 be **modified** in order to obtain a wide range of **hydrotalcites and** LDHs with different  
278 structural properties. Bontchev et al. (2003) studied the impact of several interlayer anions  
279 (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) on the physico-chemical characteristics of hydrotalcites. Moreover, this  
280 study showed the possibility to mix two different types of compensating anions to finely tune

281 the properties of these compounds. The hydrothermal synthesis of hydrotalcites with different  
282 soluble and insoluble magnesium and aluminum reactants in water has been studied by  
283 Bankauskaite and Baltakys (2011), with a fixed Mg:Al molar ratio of 3:1. **The non-formation**  
284 **of hydrotalcite phases was observed in the presence of certain reactants.** It was demonstrated  
285 that alumina and magnesium aluminum hydroxide were preferentially formed when using  
286  $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ , even after 24h of hydrothermal **treatment** at 200°C. The choice of  
287 the appropriate metal salts is the most important parameter to **be considered.** More recently,  
288 the impact of the synthesis temperature (from 35 to 140°C) has been tested by Lin et al.  
289 (2019) to synthesize CuZnAl hydrotalcite-like catalysts for arsine abatement. The authors  
290 concluded on a significant influence of the synthesis conditions on the arsine removal  
291 efficiency without clear explanation. The problem comes from the multiplicity of the  
292 parameters varied during the synthesis of the catalysts (temperature, calcination, time, molar  
293 ratios), making the results difficult to interpret. The most recent studies focus on the green  
294 synthesis of hydrotalcites and derived materials for environmental concerns, as demonstrated  
295 by Labuschagné et al. (2018) by using untreated magnesium oxide and aluminum hydroxide  
296 for hydrothermal dissolution/precipitation in water.

297 The advantages of using this synthesis process as additional treatment are the **higher LDH**  
298 **crystallinity**, crystallites **dimension**, and **purity of** the samples (Kovanda et al. 2005b; Sharma  
299 et al. 2007). In general, **a higher content of hydrotalcite is observed by increasing the**  
300 **preparation** temperature and **the time of the** hydrothermal treatment (Kovanda et al. 2005b).  
301 **Unfortunately, the energy required to heat-up the solution and the long synthesis time (from**  
302 **hours to days) represent drawbacks for the industrial implementation of the hydrothermal**  
303 **treatment.**

304

305 The recent advancements and progresses on the synthesis methodologies have been  
306 reviewed in this section. Moreover, each synthesis method has been detailed in order to  
307 enlighten the advantages and drawbacks in terms of structural and textural properties. The  
308 modulation of these features is crucial to drive the performances towards specific  
309 environmental and industrial applications. Table 1 lists the positive and negative impacts of  
310 the various synthesis routes on the structural and textural properties of LDHs.

311

## 312 2. Use of hydrotalcites and derived materials in environmental applications

313 The depletion of fossil fuels and their environmental impacts (global warming, pollution,  
314 health concerns...) are currently boosting the studies on alternative solutions and clean  
315 synthetic routes for the production of non-fossil carbon sources. Recent international  
316 conventions agreed to the Kyoto Protocol and intended to reduce by 2050 the global  
317 emissions up to 50-60% (of those measured in 2006). The necessity in finding alternative  
318 environmental applications based on easy-to-use materials becomes more than urgent. Several  
319 reactions can be performed on layered materials, but their low thermal stability makes their  
320 implementation difficult. Clay minerals are generally stable up to 200°C due to the loss of the  
321 interlayer water and the consequent irreversible degradation of the structure at temperatures  
322 higher than 200°C. The presence of specific metal elements in the structure of the LDHs can  
323 enhance their catalytic properties, depending on the applications, as mentioned by Xu et al.  
324 (2011). Moreover, due to their composition (mainly metallic cations), LDHs can be calcined  
325 to form mixed oxides presenting enhanced catalytic properties. Even if much more  
326 environmental related processes can be carried out in presence of lamellar materials, only few  
327 of them are discussed in this review. Some specific environmental application covering  
328 various technological fields have been chosen to be reported in the present review article such  
329 as the adsorption/decomposition of gaseous pollutants (CO<sub>2</sub>, NO<sub>x</sub>, and SO<sub>x</sub> adsorption, and

330 elimination of VOCs), the adsorption of pollutants in aqueous media (as the adsorption of  
331 heavy metals and dyes), and the production of green energy vectors and/or chemical building  
332 blocks (hydrogen production and formation of 5-hydroxymethylfurfural).

333

## 334 **2.1. Adsorption of atmospheric pollutants**

### 335 **2.1.1. CO<sub>2</sub> adsorption – Capture and storage**

336 Among the possible uses of hydrotalcite-like compounds and their derived mixed-oxides,  
337 CO<sub>2</sub> adsorption gains interest. Methods for safely control and dispose of carbon dioxide  
338 emissions are widely studied in the last few years, mainly due to the increase of consciousness  
339 in climate changes (Wang et al. 2017). Among all the emitted greenhouse gases, the  
340 contribution of carbon dioxide to global warming has been estimated to more than 60%. For  
341 example, steam reforming of hydrocarbons (Marquevich et al. 2001; Ashok et al. 2008; Li et  
342 al. 2011), that is the most suitable process for hydrogen production, releases high amounts of  
343 carbon dioxide. Considering the large field of materials tested for CO<sub>2</sub> capture and storage,  
344 zeolites, hydrotalcite and LDH-derived mixed oxides are widely studied thanks to their high  
345 surface area, pore structure, and charge density (Mao and Tamaura 1993; Tsuji et al. 1993;  
346 Yong et al. 2002; Wang et al. 2010; Dantas et al. 2015; Yang et al. 2019). Several reviews on  
347 CO<sub>2</sub> adsorption explain that an appropriate adsorbent should satisfy several criteria such as (1)  
348 low-cost materials, (2) fast kinetics, (3) high adsorption capacity and selectivity, and (4)  
349 thermal and chemical stability towards several cycles (Yong et al. 2002; León et al. 2010;  
350 Wang et al. 2017; Yang et al. 2019). The adsorption of CO<sub>2</sub> requires materials with large  
351 specific surface area, but also a high number of accessible basic sites. Regarding the synthesis  
352 method adapted to this application, a high number of active sites and large particles are  
353 required for better adsorption efficiency. Thus, the co-precipitation method represents the best  
354 solution to reach these requirements, especially when the LDHs structure is modified by the

355 addition of metal cations. The higher the energy of active sites, the stronger CO<sub>2</sub> interacts  
356 with the sites and remains trapped. Recently, zeolites are reported as efficient CO<sub>2</sub> adsorbents  
357 thanks to their size, charge density, and tunable chemical composition (Jiang et al. 2018; Yu  
358 et al. 2018). Hydrotalcite-based materials are thereby interesting alternative materials to  
359 zeolites, as their chemical composition can also be finely tuned. CO<sub>2</sub> adsorption performed on  
360 these materials is a natural phenomenon, as hydrotalcite can adsorb carbon dioxide thanks to  
361 the reaction of atmospheric CO<sub>2</sub> with the compensating ions present in the interlayer space.  
362 This has been evidenced by Ishihara et al. (2013) by intercalating <sup>13</sup>C carbonate anions in the  
363 hydrotalcite structure. They were exchanged with carbonate anions derived from atmospheric  
364 CO<sub>2</sub> within 1 day, showing the dynamism of the carbon cycle in nature. Moreover, these  
365 materials can be regenerated several times, without losing their adsorption capacity and  
366 selectivity towards CO<sub>2</sub>, are hydrothermally stable, and lead to fast sorption kinetics. A huge  
367 amount of studies has been performed on these materials in order to find the most efficient  
368 preparation route for CO<sub>2</sub> capture, such as impregnation of commercial hydrotalcites (Bhatta  
369 et al. 2015), synthesis of tunable Mg/Al hydrotalcites (Tsuji et al. 1993; Moreira et al. 2006;  
370 Dantas et al. 2015), and mixed oxides derived from hydrotalcites (León et al. 2010; Gao et al.  
371 2013; Radha and Navrotsky 2014; Colonna et al. 2018). Table 2 summarizes the synthesis  
372 conditions, the specific surface area, and the CO<sub>2</sub> adsorption capacity of the LDHs and related  
373 mixed oxides. It shows that the surface area is strongly linked to the CO<sub>2</sub> adsorption capacity:  
374 a higher surface area is related to an increase in the sorption capacity.

375 The preliminary studies of CO<sub>2</sub> adsorption by hydrotalcite, layered double hydroxides and  
376 related materials have been performed by Mao and Tamaura (1993) by varying the  
377 M(II)/M(III) molar ratio and consequently the layer charge of the synthesized hydrotalcites.  
378 The composition tuning resulted in a wide range of materials capable of chemically adsorb  
379 CO<sub>2</sub> with different adsorption capacities (from 0.4 to 1.5 mmol.g<sup>-1</sup>). The same year, Tsuji et



380 al. (1993) synthesized various LDHs by changing the M(II) cation nature. The selectivity  
381 towards carbon dioxide adsorption depended on the cation in the following order: Cu-Al ~  
382 Zn-Al < Co-Al < Mg-Al < Ni-Al, and was related to the thermal behavior of the various  
383 compounds. Moreover, the sorption capacities of these materials have been drastically  
384 increased by removing the carbonate counterions in the Mg-Al and Co-Al LDHs. Several  
385 years later Wang et al. (2010) studied substitution of divalent metal cations M(II) by trivalent  
386 metal cations M(III) ( $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$ ) in  $\text{CO}_2$  adsorption at high temperature,  
387 performed on calcined samples.

388 Few years after Tsuji et al. (1993), the studies about  $\text{CO}_2$  adsorption were mainly focused  
389 on industrial applications and enlightened the influence of structural parameters derived from  
390 the thermal treatment of LDHs, leading to the formation of related mixed oxides. Ram Reddy  
391 et al. (2006) showed that, depending on the applied treatment temperature, the samples  
392 exhibited different sorption capacities and reversibility. The highest sorption capacities were  
393 observed on samples pretreated at  $400^\circ\text{C}$  and a sorption temperature of  $200^\circ\text{C}$ , leading to  $\text{CO}_2$   
394 adsorption of  $0.486 \text{ mmol.g}^{-1}$ . The pretreatment conditions showed also an impact on the  
395 regeneration behavior (cycling studies). Two years later, the same team (Ram Reddy et al.  
396 2008) studied high-temperature  $\text{CO}_2$  adsorption in industrial conditions. An increase of the  
397 sorption efficiency was observed, from  $0.61$  to  $0.71 \text{ mmol.g}^{-1}$ , in presence of dry and wet  $\text{CO}_2$   
398 respectively, with more than 90% of the original capacity recovered by regeneration. Dadwahl  
399 et al. (2008) reported on the influence of the particle size on  $\text{CO}_2$  adsorption, and analyzed the  
400 formation of large particles by co-precipitation. Mixed oxides generally exhibit higher  
401 sorption capacities due to the higher specific surface area than the fresh samples, but the  
402 analysis conditions (sorption temperature, mixture of gas, etc...) affect the  $\text{CO}_2$  adsorption  
403 capacities in the same way than on non-calcined samples, as demonstrated by León et al.  
404 (2010). The obtained capacities, in the  $0.58\text{-}1.15 \text{ mmol.g}^{-1}$  range at  $50^\circ\text{C}$ , and  $0.40\text{-}0.84$

405 mmol.g<sup>-1</sup> range at 100°C, depend on the pretreatment temperature, 450 or 700°C respectively.  
406 Regarding the reversibility of these materials, the co-precipitation method at high  
407 supersaturation conditions is more adapted than that at low supersaturation, due to the  
408 formation of weaker basic sites for the latter. As previously explained, Wang et al. (2010)  
409 studied the influence of M(III) cation type towards high-temperature CO<sub>2</sub> adsorption on  
410 calcined samples at different temperatures, from 250 to 400°C. Different phases have been  
411 observed depending on the calcination temperature: MgFe<sub>2</sub>O<sub>4</sub> and MgMnO<sub>4</sub> with coexistence  
412 of MgO with the appropriate M(III) cations, whereas only MgO phases have been observed in  
413 MgAl and MgGa LDHs. Moreover, the M(III) cation nature did not affect the sorption  
414 capacity (around 0.4 mmol.g<sup>-1</sup>), except for the calcined MgGa LDH that gave lower values of  
415 CO<sub>2</sub> sorption capacity due to its lower thermal stability. Gao et al. (2013) discovered the  
416 optimal parameters to obtain hydrotalcites with improved CO<sub>2</sub> adsorption capacity: synthesis  
417 by co-precipitation method, at high supersaturation conditions, with a Mg/Al molar ratio  
418 between 3 and 3.5, and a pre-calcination temperature of 400°C (The CO<sub>2</sub> adsorption  
419 measurements were performed during 5 hours at 200°C). The operating conditions  
420 (temperature and pressure) impact the adsorption capacity of CO<sub>2</sub> too: Ramirez-Moreno et al.  
421 (2014) stated that high pressures (up to 4350 kPa) and temperatures (30-350°C) are related to  
422 higher CO<sub>2</sub> adsorption levels, with a maximum value of 5.76 mmol.g<sup>-1</sup> measured at 300°C  
423 and 3450 kPa. Higher values can be reached at higher temperatures and pressures, and related  
424 to structural changes in the LDHs framework (formation of magnesium oxides and periclase  
425 for example).

426 The most recent researches focus on modifications of the structure of LDHs synthesized by  
427 co-precipitation in order to increase their CO<sub>2</sub> adsorption capacity. Similar to simple ion-  
428 exchange reaction, the potassium impregnation consists in putting the synthesized materials  
429 into a solution with a defined concentration of potassium salt during few hours, followed by

430 the washing of the salt excess.  $K_2CO_3$  impregnation seems to increase the number of surface  
431 active sites despite a decrease in the specific surface area. This impregnation leads to high  
432 adsorption capacities, as demonstrated by Bhatta et al. (2015): values up to  $1.10 \text{ mmol.g}^{-1}$  at  
433  $300^\circ\text{C}$  for the initial sorption cycle, and of  $0.42 \text{ mmol.g}^{-1}$  for the following 9 cycles of  
434 adsorption/desorption were measured. Polymers addition can modify the textural properties of  
435 layered materials and contribute to the enhancement of the  $CO_2$  sorption capacity, as showed  
436 by Dantas et al. (2015) by the addition of a co-polymer that increased the  $CO_2$  uptake from  
437  $0.72$  to  $1.36 \text{ mmol.g}^{-1}$ . Tang et al. (2018) increased the basal spacing of LDHs by exchanging  
438 anions with dodecylsulfonate ions in order to chemically graft (3-aminopropyl)triethoxysilane  
439 (APS) and enhance the  $CO_2$  sorption capacity (up to  $2.09 \text{ mmol.g}^{-1}$  at  $50^\circ\text{C}$ ). The presence of  
440 amino groups in the interlamellar space strongly contributed to the capture of carbon dioxide  
441 through the zwitterion mechanism and weak bonding. By optimizing the synthesis parameters,  
442 Thouchprasitchaia et al. (2018) obtained a series of calcined teraethylenepentamine (TEPA)-  
443 supported hydrotalcites. At first, increasing the TEPA loading led to higher adsorption  
444 capacities, explained by the availability of more basic sites with a higher affinity for  $CO_2$ . A  
445 too high TEPA content resulted in the decrease of the sorption capacity due to the steric  
446 hindrance of TEPA that blocks the access of  $CO_2$  to the sorption sites.

447 Among the large panel of industrial applications, sorption enhanced reactions processes  
448 (SERP) gained huge interest in the last decade, especially thanks to novel modifications  
449 introduced into LDHs structure. SERPs have been developed for the efficient conversion of  
450 methane to hydrogen. The main drawback of this process is the formation and release of large  
451 amounts of  $CO_2$ , then materials with high carbon dioxide sorption capacity are crucial for this  
452 application. The first amine modifications of LDHs for  $CO_2$  adsorption performance towards  
453 SERP applications have been performed by Wang et al. (2012b, a) via two different routes:  
454 anionic surfactant-mediated synthesis and exfoliation. In the first case, low  $CO_2$  adsorption

455 capacities (up to  $0.6 \text{ mmol.g}^{-1}$ ) have been recorded, mainly due to the presence of Sodium  
456 Dodecyl Sulfate (SDS) in the interlayer space. SDS can be then removed using  
457 monoethylamine extraction (ion exchange reaction), leading to higher sorption values  
458 (between  $1.15$  and  $1.4 \text{ mmol.g}^{-1}$ ) (Fig6.). On the opposite, the exfoliation route in the presence  
459 of toluene allows to graft amine groups on the surface of LDHs giving high sorption  
460 capacities towards  $\text{CO}_2$  (around  $1.7 \text{ mmol.g}^{-1}$  at  $80^\circ\text{C}$ ). The two studies underline the  
461 importance of the interlayer space in LDHs: sodium dodecyl sulfate and aminosilanes  
462 molecules present in this area cover the main part of the basic sites involved in the  $\text{CO}_2$   
463 adsorption, consequently lowering the sorption capacity. It is important to consider the steric  
464 hindrance when considering lamellar materials. Most of the time, K-promoted hydrotalcites  
465 are interesting adsorbents in SERP, as the potassium presence leads to sorption capacities  
466 higher than  $1 \text{ mmol.g}^{-1}$ , as demonstrated by Wu et al. (2013). Moreover, the adsorption  
467 capacity and kinetics were not affected even after 10 cycles, which is interesting for SERP  
468 applications. Coenen et al. (2017b, a) also published about K-promoted hydrotalcites in a  
469 series of publications for sorption-enhanced water-gas shift. This article points out the  
470 importance of chemisorbed  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , strongly linked to the specific adsorption sites. The  
471 presence of four different adsorption site types was identified: two site types with high  
472 affinity for  $\text{CO}_2$ , one for  $\text{H}_2\text{O}$  and one on which  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can competitively adsorb. The  
473  $\text{CO}_2$  adsorption sites can be easily regenerated in presence of  $\text{N}_2$ , and the cycling is favored at  
474 high temperatures. In the most recent study of the same group (2018), the adsorption  
475 processes were studied by infrared spectroscopy, showing once again the presence of the four  
476 types of adsorption sites. The presence of water molecules enables the decomposition of the  
477 strong bonds with carbonate sites, ameliorating the cycling behavior. The comparison  
478 between LDHs and zeolites has been recently performed by Megías-Sayago et al. (2019) and  
479 the importance of the surface area was evidenced. While zeolites exhibited surface areas

480 around  $360 \text{ m}^2.\text{g}^{-1}$  and adsorb  $\text{CO}_2$  up to  $1.142 \text{ mmol}.\text{g}^{-1}$ , MgAl and CaAl LDHs presented  
481 lower specific surface areas ( $50$  and  $21 \text{ m}^2.\text{g}^{-1}$ ) and adsorb carbon dioxide up to  $0.68$  and  $0.10$   
482  $\text{mmol}.\text{g}^{-1}$ , respectively.

483 Table 3 and Fig7. display the  $\text{CO}_2$  adsorption capacities of various LDHs reported in the  
484 literature. Non-modified materials exhibit values between  $0.5$  and  $1 \text{ mmol}.\text{g}^{-1}$ , while modified  
485 LDHs present much higher values, up to  $6.1 \text{ mmol}.\text{g}^{-1}$ .

486

487 As demonstrated by various studies, LDHs are interesting alternatives to zeolites and  
488 activated carbons for  $\text{CO}_2$  adsorption and storage. Adsorption capacities between  $0.5$  and  $6$   
489  $\text{mmol}.\text{g}^{-1}$  could be measured depending on the structural modifications, the pre-treatments  
490 performed prior the adsorption, and the configuration of the adsorption experiments  
491 (operating temperature and pressure, gas composition, time of adsorption). Older papers  
492 stated on the optimal synthesis conditions and co-precipitation performed at high-  
493 supersaturation seems to be the most adapted method. More recent researches focus on  
494 sorption-enhanced reaction processes, due to the needs of minimize the release of  $\text{CO}_2$  while  
495 producing hydrogen from methane. Regarding the synthesis process, co-precipitation allows  
496 to obtain large and crystalline particles, increasing the amount of basic sites that are required  
497 to reach large amounts of  $\text{CO}_2$  adsorbed. The calcination of such materials leads to the  
498 formation of mixed oxides with higher surface areas, and consequently an increased number  
499 of basic sites. One of the most important parameter to take into account in this application is  
500 the specific surface area that is strongly related to the  $\text{CO}_2$  adsorption capacity. Moreover,  
501 Table 2 evidences slightly higher adsorption capacities for the materials synthesized by co-  
502 precipitation at high supersaturation conditions than for those prepared at low supersaturation  
503 conditions, except in the samples modified with TEPA (up to  $6 \text{ mmol}.\text{g}^{-1}$ ), as shown by

504 Thouchprasitchaia et al. (2018). However, the commercial hydrotalcite tested by Wu et al.  
505 (2013) exhibits similar adsorption capacities than the modified LDHs.

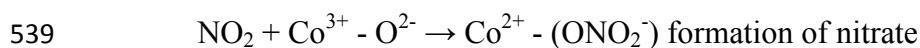
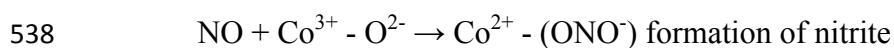
506

### 507 **2.1.2. NO<sub>x</sub> and SO<sub>x</sub> adsorption**

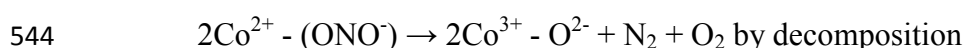
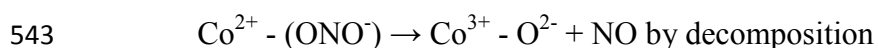
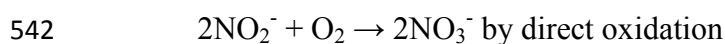
508 Among the wide family of atmospheric pollutants, nitrogen and sulfur-based molecules are  
509 emitted from power plants, petroleum refinery, and vehicle engines (Yang et al. 2014).  
510 Nitrogen oxides (NO<sub>x</sub>) and Sulfur oxides (SO<sub>x</sub>, a mixture of SO<sub>2</sub> and SO<sub>3</sub>) are released into  
511 the atmosphere with exhausted gases, causing environmental and climatic concerns such as  
512 acid rains, photochemical smog and human diseases (asthma for example) (Corma et al. 1997;  
513 Yu et al. 2006; Yang et al. 2014; Wang et al. 2018). The control of these emissions is  
514 becoming mandatory due to the increased awareness towards the climate change. Moreover,  
515 several laws and strict regulations have been put into place in the last decade, and encourage  
516 researches on more efficient ways to reduce them. Several depollution processes have been  
517 developed with good results, such as the direct decomposition (Yokomichi et al. 1996;  
518 Imanaka and Masui 2012; Gunugunuri et al. 2018; Gunugunuri and Roberts 2019), adsorption  
519 (Mahzoul et al. 1999; Sedlmair et al. 2003; Atribak et al. 2009), Selective Catalytic Reduction  
520 (SCR) (Lukyanov et al. 1995; Forzatti et al. 2010; Gao et al. 2018; Gramigni et al. 2019; Wu  
521 et al. 2019b; Li et al. 2019b), and NO<sub>x</sub> Storage and Reduction (NSR) (Castoldi et al. 2006;  
522 Breen et al. 2008; Sakano and Kawamura 2018; Umeno et al. 2019). LDHs are interesting due  
523 to their efficiency in a wide range of application, as catalysts and adsorbents. In recent years,  
524 hydrotalcite-like compounds have exhibited good NO<sub>x</sub> and SO<sub>x</sub> adsorption capacities. This  
525 chapter is dedicated to the adsorption and removal of these atmospheric pollutants by LDHs  
526 and related mixed oxides; the synthesis conditions of each LDH are reported in the Table 4  
527 with the associated structural modifications.

528

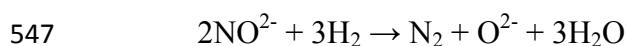
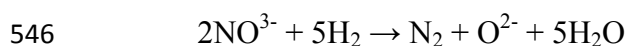
529 The most important part of the emitted NO<sub>x</sub> comes from the Fluid Catalytic Cracking  
530 (FCC) method employed by refinery processes to convert heavy distillates into lighter ones,  
531 such as gasoline and diesel. In this process, the catalyst gets progressively covered with coke  
532 and needs to be reactivated by burning and oxidizing the coke in a regenerator unit, NO<sub>x</sub> is  
533 here produced (Chaparala et al. 2015). The catalysts are reactivated by reduction at 750°C, so  
534 most of the studies are focused on experiments under these conditions. The storage and  
535 catalytic reduction of NO<sub>x</sub> compounds on the surface of LDH catalysts occurs firstly on the  
536 catalytic sites to form nitrites and nitrates, as shown in Fig8, and according to the following  
537 reactions (Guo et al. 2018):



540 Nitrites are unstable on the active sites and are then oxidized to nitrate in the presence of O<sub>2</sub>  
541 or decomposed via the following reactions:



545 The stored NO<sub>x</sub> is finally converted to N<sub>2</sub> and H<sub>2</sub>O by reacting with H<sub>2</sub> at 350°C:



548 The first catalytic removal of NO<sub>x</sub> using copper-containing LDHs-derived mixed oxides  
549 has been reported in the late 90s by Corma et al. (1994). The possibility to incorporate the  
550 catalyst in the FCC units was explored, because NO<sub>x</sub> can be decomposed by the catalyst  
551 reduced under a reductive atmosphere at 550°C, conditions close to those present in the  
552 regenerator unit of a FCC plant. The simultaneous removal of NO<sub>x</sub> and SO<sub>x</sub> in conditions  
553 close to those of the regenerator unit was investigated: Cu-mixed oxides derived from

554 hydrotalcite showed to be able to remove both SO<sub>2</sub> (via an oxidation or reduction reaction)  
555 and NO (via reduction and/or decomposition) at the same time in the presence of small  
556 amounts of O<sub>2</sub> (between 0 and 1.5%). Doping the catalysts with transition metals, such as  
557 cobalt, is of great interest on the storage capacity of NO<sub>x</sub> in hydrotalcites; Palomares et al.  
558 (1999) studied the catalytic activity of CoMgAl mixed oxides derived from hydrotalcites.  
559 Besides increasing the surface area by addition of cobalt, the authors concluded that in  
560 presence of O<sub>2</sub> (up to 1%) the catalyst is able to efficiently remove the atmospheric pollutants.  
561 In presence of oxygen in the feed and at 750°C, cobalt-containing materials showed to be  
562 more selective towards NO reduction than Cu-based compounds. Almost 100% of NO  
563 conversion was reached in less than 50s and remained stable during time. Yu et al. (2006)  
564 prepared a range of Co<sub>x</sub>Mg<sub>3-x</sub>/Al hydrotalcite-like compounds, where *x* varied from 0 (pure  
565 MgAl hydrotalcite) to 3 (pure CoAl hydrotalcite). Despite the decrease of the specific surface  
566 area while increasing the cobalt content, the results showed that higher storage capacities of  
567 NO<sub>x</sub> were reached at low temperatures with mixed oxides of intermediate Co concentrations  
568 (0.22 mmol.g<sup>-1</sup> at 100°C for *x* = 0.5). The pure phases exhibited the lowest storage capacities,  
569 around 0.14 mmol.g<sup>-1</sup> for MgAl and CoAl hydrotalcites. These results are explained by the  
570 increase in the pore size, from 11.6 nm in the pure MgAl mixed oxides to 24.8 nm for the  
571 samples with the highest cobalt concentration. Similar experiments were performed the next  
572 year by the same team (Yu et al. 2007) with two catalysts: Ca<sub>2</sub>CoAl-oxide and  
573 Ca<sub>2</sub>CoLa<sub>0.1</sub>Al<sub>0.9</sub>-oxide, derived from their LDH precursors. NO<sub>x</sub> storage capacities up to 0.65  
574 mmol.g<sup>-1</sup> at 250°C were measured. Noble metals such as platinum, palladium and ruthenium  
575 have also been intensively studied towards the storage of NO<sub>x</sub> due to their high catalytic  
576 redox properties. Cheng et al. (2004) worked on Pt/MgAl oxides: MgAl oxides supports with  
577 different molar ratios were obtained by calcination of hydrotalcites, while platinum cations  
578 were incorporated by incipient wetness impregnation. The authors concluded that by

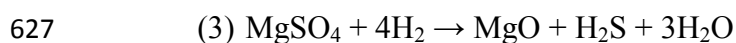
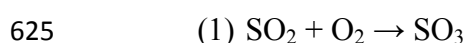


579 **increasing** the Mg/Al molar ratio in the initial hydrotalcites, the stored amount of NO<sub>x</sub> at  
580 350°C **was enhanced**. **Moreover**, the addition of platinum **as active phase** greatly improved  
581 the **NO<sub>x</sub>** storage capacity (from 0.06 to 0.50 mmol.g<sup>-1</sup>). NO<sub>x</sub> are stored as nitrates that are  
582 more stable over Pt/Mg oxides than over Pt/MgAl oxides. A similar approach has been  
583 performed by Silletti et al. (2006) with Pd/MgAl oxides. Additional adsorption sites **were**  
584 **created, bringing to an increase of 70% in** the adsorption capacity, when compared to the  
585 MgAl oxides (according to the reaction  $\text{PdO}_{(s)} + \text{NO}_2 \rightarrow \text{Pd}(\text{NO}_3)_{(s)}$ ). Finally, RuMgAl oxides  
586 have been reported by Li et al. (2007) and exhibited good performances, with a maximum  
587 storage **capacity** of 0.22 mmol.g<sup>-1</sup> at 350°C.

588 The most recent researches **focus** on low temperature storage and release of NO<sub>x</sub> between  
589 150 and 300°C, as reported by Cui et al. (2019) with manganese-doped mixed oxides derived  
590 from hydrotalcite precursors. The incorporation of manganese provokes changes in the crystal  
591 phases with formation of Mn<sub>3</sub>O<sub>4</sub> and MgMn<sub>2</sub>O<sub>4</sub> spinel besides brucite. These changes result  
592 in **the** increase of the surface area (from 108 to 139 m<sup>2</sup>.g<sup>-1</sup>) and **of** the pore size (from 14 to 23  
593 nm), while the presence of manganese favors the oxidation of NO during adsorption. The  
594 largest adsorption capacity of 0.426 mmol.g<sup>-1</sup> at 300°C **was** obtained in **the** presence of 15  
595 wt% of Mn, as **reported in Fig9. The efficiency of LDHs containing various metallic elements**  
596 **towards the adsorption of NO<sub>x</sub> pollutants has also been reported by Li et al. (2019b) on a**  
597 **novel NiMnTi mixed oxide, showing high surface area and strong reducibility, resulting in**  
598 **strong surface acidity. Moreover, manganese, nickel and titanium give interesting redox**  
599 **properties to LDHs and gained interest in the last years (Wang et al. 2018; Wu et al. 2019b; Li**  
600 **et al. 2019b).** The recent study performed by Kameda et al. (2019) **presents** another approach  
601 on the adsorption of NO<sub>x</sub>. **The employed catalysts were fresh MgAl hydrotalcites that could**  
602 **be simply** recycled by anion desorption in a solution of Na<sub>2</sub>CO<sub>3</sub>. Low NO removal rate was

603 observed, but the removal of NO<sub>2</sub> was possible, and stable at around 50% removal degree,  
604 during 3 cycles.

605 Concerning SO<sub>x</sub> removal for industrial applications, several patents are related to the use of  
606 hydrotalcites in FCC units (Pinnavaia et al. 1991, 1992; Vierheilig 2003). These compounds  
607 are emitted during the oxidative regeneration process of the catalysts at 700-800°C. The  
608 general FCC process applied to the SO<sub>x</sub> removal is schematized in Fig10. Regarding the  
609 process conditions, several requirements are needed to trap SO<sub>x</sub> (Mathieu et al. 2013): (1) a  
610 high thermal stability of the adsorbent under FCC conditions, (2) the ability to oxidize SO<sub>2</sub> to  
611 SO<sub>3</sub>, (3) the possibility to regenerate the adsorbent under a reductive flow of H<sub>2</sub> to release  
612 sulfur as H<sub>2</sub>S, (4) the possibility to strongly chemisorb SO<sub>x</sub> in the regenerator unit, and (5) the  
613 absence of negative impact of the adsorbent on the conversion and selectivity of FCC  
614 products. LDHs and hydrotalcites can answer to these requirements: they have the ability to  
615 form mixed oxides of the desired elements, stable at high temperatures, and are able to be  
616 regenerated in water. The catalytic activity of such compounds strongly depends on the  
617 surface area (related to the number of active sites) and on the type of metallic cation  
618 employed (for their ability to react with SO<sub>x</sub> compounds) (Cantú et al. 2005; Valente and  
619 Quintana-Solorzano 2011; Mathieu et al. 2013). The first experiments, focused on MgO,  
620 Al<sub>2</sub>O<sub>3</sub> and MgAl spinels derived from pure MgAl hydrotalcites, showed very low  
621 performances; MgO forms stable MgSO<sub>4</sub> compounds and Al<sub>2</sub>O<sub>3</sub> forms Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> that is very  
622 unstable at these temperatures, leading to the release of sulfate species in the regenerator (Yoo  
623 et al. 1992). Three basic reactions are involved in the removal of SO<sub>x</sub> in the FCC regenerators  
624 (Yoo et al. 1992):



628 Based on these equations, several oxides derived from hydrotalcites and LDHs have been  
629 tested in the last decade. The most studied samples were prepared by addition of transition  
630 metals similar to those used in the NO<sub>x</sub> removal processes. Cantú et al. (2005) reported for  
631 example on mixed oxides derived from MgAlFeCe hydrotalcites. Despite the lower surface  
632 area and low SO<sub>2</sub> adsorption capacity, the oxides containing iron and cerium presented an  
633 interesting resistance to deactivation. The addition of cerium increased the adsorption rates  
634 and reduced the saturation times, while a limited amount of iron improved the catalytic  
635 regeneration of SO<sub>x</sub> adsorbents. A similar study was then performed by Valente and  
636 Quintana-Solorzano (2011) in partial and full combustion conditions (used for regeneration).  
637 The performances of mixed oxides derived from MgAlFeCe hydrotalcites were compared to  
638 those of a commercial catalyst. Hydrotalcites showed a lower deactivation rate and the  
639 necessity to use 33% less material than the commercial catalyst. However, only very few  
640 recent papers report on the adsorption and removal of SO<sub>x</sub> by LDHs-based materials. The  
641 most recent researches focus on catalysts capable of simultaneously adsorb SO<sub>x</sub> and NO<sub>x</sub>  
642 (Kameda et al. 2011, 2019a, 2020).

643

644 NO<sub>x</sub> and SO<sub>x</sub> are dangerous compounds formed during the regeneration process of the  
645 catalysts employed in the FCC units. Due to their toxicity, their removal has been widely  
646 studied. Hydrotalcites and mixed oxides derived from LDHs, in particular those containing  
647 transition metals (copper or cerium) or noble metals (platinum, palladium or ruthenium) have  
648 been considered for this application. High specific surface area, large pore sizes and improved  
649 catalytic properties have been obtained by the addition of metallic cations, leading to  
650 interesting results in NO<sub>x</sub> and SO<sub>x</sub> adsorption in regeneration conditions (around 750°C  
651 under a reducing atmosphere). Co-precipitation was the most widely used synthesis method  
652 for LDHs, allowing to obtain high specific surface areas, pore sizes and a high number of

653 active sites. Higher adsorption capacities were reached with co-precipitated LDHs (0.10-0.65  
654 mmol.g<sup>-1</sup>), compared to commercial samples (up to 0.06 mmol.g<sup>-1</sup>), as shown by the Table 3.  
655 The specific surface areas remain in the same range of values (between 100 and 250 m<sup>2</sup>.g<sup>-1</sup>)  
656 thanks to the modifications performed on the commercial LDHs, which evidences that the  
657 specific surface area is not the only parameter to be taken into consideration for increasing the  
658 performances in this application. Some additional studies have been performed on the  
659 simultaneous adsorption of NO<sub>x</sub> and SO<sub>x</sub> in order to obtain a polyvalent compound stable  
660 under the conditions of the FCC regenerator units (Kameda et al. 2011, 2019a, 2020).

661

### 662 **2.1.3. VOCs total decomposition**

663 Volatile Organic Compounds (VOCs) give origin to an important class of organic  
664 pollutants, such as toluene, ethanol, methanol, acetone and ethylene (Bahranowski et al. 1999;  
665 Carpentier et al. 2002; Gennequin et al. 2010a; Mrad et al. 2015; Kamal et al. 2016). They are  
666 emitted from various industrial processes and transport vehicles and represent a serious  
667 environmental problem. VOCs are the major contributors to air pollution due to their direct  
668 toxic and carcinogenic properties, or indirect contribution to ozone formation. The  
669 decomposition of VOCs is thereby crucial for an environmental point of view. VOCs removal  
670 requires technologies working under hard conditions (temperatures up to 1100°C and  
671 presence of toxic products). The possibility to eliminate VOCs at temperatures lower than  
672 those reached during classical combustion is of great interest. Catalytic total combustion of  
673 VOCs is then one of the most effective and economically attractive treatment explored in the  
674 last decades (Bahranowski et al. 1999; Mikulová et al. 2007; Dula et al. 2007; Tanasoi et al.  
675 2009; Palacio et al. 2010; Kamal et al. 2016). Most catalysts used for the total decomposition  
676 of VOCs contain noble metals, such as palladium and gold. Mixed oxides based on transition  
677 metals have been also successfully tested with similar activity, as cheaper alternative. The

678 catalysts must present a high thermal stability and a large number of active sites. Co-  
679 precipitation is once again the most adapted method to obtain the desired properties. It permits  
680 to easily substitute cations in the structure and to promote the formation of large platelets with  
681 a high number of active sites. The synthesis conditions of all the samples cited in this part  
682 have been listed in Table 5.

683  
684 Similarly to CO<sub>2</sub> adsorption, the total decomposition of VOCs by hydrotalcites and LDHs  
685 has been studied on various catalysts presenting different substitutions, and in different  
686 analytical conditions. The tests were mainly focused on the total decomposition of toluene or  
687 ethanol. The first experiments focused on the elimination of VOCs by mixed oxides derived  
688 from LDHs have been performed in the late 90s, even if the reaction was already known since  
689 many decades. Moderated temperatures, around 200°C, are required for this catalytic reaction.  
690 The catalysts are mixed oxides and amorphous phases obtained by calcination of LDHs at  
691 high temperature. Bahranowski et al. (1999) reported on the impact of Cu(II) and Cr(III)  
692 cations in mixed oxides derived from parent LDHs on the total oxidation of toluene and  
693 ethanol performed at various temperature. The authors observed that the purity and  
694 crystallinity of the materials depends on the initial Cu:Cr molar ratio, and that the catalyst  
695 derived from the CuCr hydrotalcite, with an initial Cu:Cr molar ratio of 2, gave the best  
696 catalytic performances in both toluene and ethanol oxidations. A similar study, focused on the  
697 crystallinity of the LDH precursors, was performed few years later by Mikulova et al. (2007)  
698 on calcined NiAl LDHs. The analyses showed slightly lower catalytic activities than for CuCr  
699 hydrotalcites-derived oxides synthesized by Bahranowski et al. (1999) towards toluene  
700 oxidation. In ethanol oxidation, the formation of reaction intermediates, such as acetaldehyde,  
701 could be avoided by increasing the reaction temperature. Cobalt-containing hydrotalcite  
702 precursors with different compositions were tested by Gennequin et al. (2009, 2010b). They

703 showed interesting activities in toluene oxidation, especially the sample containing the highest  
704 amount of cobalt, that presented the highest specific surface area, well dispersed oxides and  
705 lower presence of cobalt aluminate species. Fig11. shows the impact of the calcination  
706 temperature of Co-containing hydrotalcites on the toluene conversion. The same research  
707 group also performed studies focused on the memory effect of hydrotalcite (Gennequin et al.  
708 2010a), their ability to regenerate their structure by simple wetting or impregnation. In this  
709 case, cobalt impregnation led to the partial regeneration of the LDH structure and improved  
710 the toluene oxidation activity.

711 Palacio et al. (2010) studied the impact of different trimetallic hydrotalcites (ZnCuAl and  
712 MnCuAl), after calcination at 450°C, over the oxidation of toluene. The MnCuAl catalysts  
713 showed to be the most efficient (Mrad et al. 2015). Dula et al. (2007) performed a similar  
714 study on MgAlMn-oxide (obtained from calcination of the parent LDH). The catalyst was  
715 more active than MnO<sub>4</sub>-impregnated MgAl LDH for the combustion of toluene under air.  
716 This behavior can be explained by the enhanced presence of redox sites on the surface of the  
717 as-generated mixed oxide particles. Methane is a bit more difficult to oxidize due to its high  
718 inertness: its complete oxidation occurs at much higher temperature than toluene and ethanol,  
719 as studied by Tanasoi et al. (2009), with 50% of methane decomposition at 480-490°C over a  
720 calcined Cu-containing MgAl-LDH catalyst. This work shows that the catalytic activity is  
721 dependent of the reducible amount of copper in the catalyst. Aguilera et al. (2011) performed  
722 a more complete study on the total oxidation of 3 different VOCs: butanol, ethanol and  
723 toluene by copper-manganese and cobalt-manganese catalysts derived from the parent LDHs.  
724 The catalytic activity depended on the VOC type, and the activity scale was the following for  
725 both catalyst: butanol < ethanol < toluene. Some other studies (Chmielarz et al. (2012))  
726 focused on mono-carbon VOCs (methane, methanol, and formic acid). The calcination  
727 temperature had a direct impact on the complete oxidation: the presence of cobalt phases,

728 obtained at high calcination temperatures (up to 800°C), induced higher catalytic activities in  
729 conversions of methanol and formic acid.

730 Other modifications, such as the type of interlayer anion or the use of a support, can be  
731 introduced in the catalyst conception. Carpentier et al. (2002) demonstrated that the  
732 substitution of carbonate anions by palladium complexes in the interlayer space of Mg/Al  
733 hydrotalcites improves the catalytic activity. Kovanda and Jirátová (2011a, b) supported  
734 several mixed oxides, derived from hydrotalcites, on Al<sub>2</sub>O<sub>3</sub>/Al or calcined alumina, and  
735 resulted in interesting catalytic activities with the production of side products such as  
736 acetaldehyde. Spinel phases identified in the calcined samples are also linked to the high  
737 conversion values observed.

738

739 Similar to CO<sub>2</sub> adsorption, the total elimination of VOCs remains a very important  
740 environmental issue to be solved. Most of the LDHs used in this field are synthesized by co-  
741 precipitation method that makes possible the structural substitution of metallic cations, such  
742 as chromium or copper, in order to increase the catalytic activity. Differently than for the  
743 samples used in NO<sub>x</sub> and SO<sub>x</sub> adsorption, the materials prepared for VOCs elimination, and  
744 that contains metal cations in the structure, show similar specific surface area values (between  
745 10 and 250 m<sup>2</sup>.g<sup>-1</sup>) when obtained at low or high supersaturation conditions (Table 5). The  
746 main differences in the samples comes essentially from the inserted metallic cation and the  
747 thermal treatment (temperature and duration). According to the literature, the total elimination  
748 of VOCs by LDH-based materials is very promising.

749

## 750 **2.1.Adsorption of aqueous pollutants**

751 Nowadays the pollution of water is mainly deriving from several industrial effluents  
752 (papermaking, textiles and dyeing for example) and agricultural activities (Chuang et al.

2008; Tzompantzi et al. 2011; Ali 2012). Some of the pollutants released in nature can move into soils and plants. Their high mobility provokes a global concern due to their significant impact on the human health, biotoxicity and carcinogenic effects (Lv et al. 2006; Chuang et al. 2008). As water resource is a fundamental resource on earth and remains rare in some regions, the need to find cheap and efficient depollution processes has increased worldwide. The wide family of aqueous pollutants includes inorganic pollutants (toxic heavy metals such as As, Pb, Cd, Ni, Zn and Cr for example (Lehmann et al. 1999; Yang et al. 2005; El-Sayed et al. 2016; Wan et al. 2017)), organic pollutants (mainly dyes from paper and textile industries (Tzompantzi et al. 2011; Ahmed and Gasser 2012; de Sá et al. 2013; Shan et al. 2014), but also drugs and pharmaceuticals (Chuang et al. 2008; Zhao et al. 2015; Yu et al. 2017)). Many approaches have been proposed for water treatment, including coagulation (Zou et al. 2016a, b), precipitation (Barrera-Díaz et al. 2012; Cheng et al. 2015), sedimentation (Rubí et al. 2009; Guo et al. 2009), sorption (Karickhoff 1984; Fosso-Kankeu et al. 2010; Alila et al. 2011), and ion exchange (Leinonen et al. 1994; Mazur et al. 2016). Regarding the literature, sorption is the most versatile process for removing pollutants at relatively low concentrations, and it is environmentally friendly. This process includes the use of lamellar materials such as clay minerals (Milutinović-Nikolić et al. 2014, p. 99; Wang et al. 2015; Yang et al. 2015) and LDHs (Yang et al. 2005; Chuang et al. 2008; Ahmed and Gasser 2012; Zou et al. 2017), but also activated carbons (Beita-Sandí et al. 2016; Bedin et al. 2016), graphene (Li et al. 2012; Song et al. 2015; Sun et al. 2017), and metal oxides (Tzompantzi et al. 2011; Cheng et al. 2015; Zou et al. 2017). The main obstacle using these materials is their relatively low adsorption capacity, so the majority of the studies is focused on increasing their efficiency. This part of the review discusses about the last advances in the use of LDHs and derived mixed oxides in the adsorption and removal of aqueous pollutants in the last decades. The synthesis parameters of the materials described in this part are listed in the Table 6.



778 Inorganic pollutants are mainly constituted of heavy metals such as arsenic, lead, cadmium,  
779 nickel, zinc and chromium. Their toxicity has been well documented, and their removal  
780 gained large focus in the last decades (Barrera-Díaz et al. 2012). Thanks to their accessible  
781 and expansible interlayer space, LDHs are interesting adsorbents and ion exchangers of these  
782 pollutants. Their use has been firstly documented in the late '90s and the performances often  
783 compared to those of other inorganic sorbents, such as activated carbons and metal oxides  
784 (Lehmann et al. 1999). Pure MgAl hydrotalcites generally exhibit interesting removal  
785 capacities, up to 50% of Cr(VI) and 100% Zn(II) at pH 4, and are able to act as anion-  
786 exchangers (in the interlayer space) and proton-acceptors (presence of carbonate ions  $\text{CO}_3^{2-}$ ).  
787 Moreover, an increase of the solution pH leads to a partial dissolution of the LDH structure  
788 and causes the precipitation of cationic metal species increasing the overall removal of  
789 inorganic pollutants. These materials are also efficient towards the removal of trace levels of  
790 pollutants, such as arsenic and selenium for example, as described by Yang et al. (2005) by  
791 using calcined and uncalcined MgAl hydrotalcites. The adsorption values of uncalcined  
792 samples are strongly influenced by the pH of the solution, while no influence of pH was  
793 measured on calcined samples (Fig12). In both cases, the desorption of As(V) and Se(IV)  
794 strongly depended on the anion species, with maximum amounts of 100ppm in presence of  
795  $\text{HPO}_4^{2-}$  and 1000ppm with  $\text{SO}_4^{2-}$ , and with desorption yields close to 100%. Several  
796 parameters influence the removal capacity by LDHs, such as the pH of the solution, the initial  
797 pollutant concentration, and the adsorbent dosage (Lv et al. 2006). Similar to other  
798 applications previously discussed, the addition of metallic cations in the structure of LDHs  
799 and derived mixed oxides increases the specific surface area and the pore volume of these  
800 materials, leading to better sorption capacities. El-Sayed et al. (2016) reported the efficiency  
801 of MgAlZn mixed oxides derived from calcined hydrotalcites and observed adsorption  
802 capacities up to 1.98 and 1.19  $\text{mmol.g}^{-1}$  for Co(II) and Ni(II), respectively. A more recent

803 study showed the positive impact of incorporating LDHs onto a matrix of other nature. Once  
804 incorporated into biochar (Xue et al. 2016), MgFe LDHs can uptake nitrates with values up to  
805 0.4 mmol.g<sup>-1</sup>, which are higher than those obtained on MgFe LDHs alone (0.08 mmol.g<sup>-1</sup>) or  
806 on activated carbons (0.15 mmol.g<sup>-1</sup>). Chitosan has also been tested due to the possibility to  
807 adsorb large amounts of metal ions. Indeed, TiFe LDHs modified with chitosan can exhibit  
808 high removal capacities (close to 100%) for cadmium and phosphate in mono- and multiple-  
809 pollutant solutions (Mahmoud et al. 2017). The use of hierarchical SiO<sub>2</sub>@LDHs on SiO<sub>2</sub>  
810 spheres has been studied by Yang et al. (2017) to remove uranium (U(VI)) from aqueous  
811 solution. Thanks to the complexations and electrostatic interactions with the abundant  
812 oxygen-containing functional groups, a maximum sorption capacity of 1.27 mmol.g<sup>-1</sup> was  
813 reported. Similar adsorption capacities have been reported by Zou et al. (2017) using CaMgAl  
814 LDHs and derived mixed oxides, with values depending on the calcination temperature of the  
815 LDH: from 0.55 (for uncalcined LDH) up to 2.04 mmol.g<sup>-1</sup> (for calcined LDH at 500°C).

816 Another family of pollutants regroups the organic aqueous pollutants (pharmaceuticals and  
817 molecules with high molecular mass) that are released in nature by chemical industries,  
818 creating serious environmental issues due to their high toxicity, even at low concentrations  
819 (Chuang et al. 2008; Tzompantzi et al. 2011). The interest in finding new sorbent for  
820 removing such compounds from water increased in the last ten years, even if the toxicity and  
821 the possibility to adsorb these pollutants by natural materials is known since the '80 (Zepp  
822 and Schlotzhauer 1981; Karickhoff 1984). Sorption is one of the most common treatment to  
823 remove organic pollutants from nature; LDHs and derived mixed oxides are great candidates  
824 thanks to the high sorption capacity in the interlayer region, the large specific surface area and  
825 the presence of reactive surfaces (Pavan et al. 1999, 2000; Seki and Yurdakoç 2005; Chuang  
826 et al. 2008). Phenolic compounds are the most common organic water pollutants and their  
827 adsorption has been widely studied. Tzompantzi et al. (2011) reported on the fast

828 photocatalytic degradation of phenols in the presence of ZnAl mixed oxides derived from  
829 LDHs. The photodegradation rate is maximized thanks to the electron transfer from  $Zn^{2+}$  to  
830  $Al^{3+}$ . The removal of phenol molecules by photocatalysis has also been reported by Seftel et  
831 al. (2015) using  $TiO_2$  deposited on various LDHs matrices presenting different cation  
832 compositions ( $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$  and  $Ti^{4+}$ ). The specific surface area depended on the  
833 cations (from  $5\text{ m}^2\cdot\text{g}^{-1}$  with Cu-substituted LDH to  $199\text{ m}^2\cdot\text{g}^{-1}$  for Fe-substituted LDH), and  
834 almost 90% efficiency towards phenol adsorption by all the  $TiO_2$ -modified LDHs was  
835 obtained after 5h of UV and visible light irradiation.

836 Concerning dyes elimination from aqueous solutions, a number of technologies were  
837 recently developed, such as the adsorption by activated carbon (Özacar and Şengil 2002) or  
838 the nanofiltration (Koyuncu 2002; Lau and Ismail 2009). However, the formation of sludges  
839 in large quantities or the high operation cost make them not suitable for industrial and large-  
840 scale applications (Ahmed and Gasser 2012). The low cost and regeneration properties of  
841 LDHs make the use of such materials interesting, as demonstrated by Ahmed and Gasser  
842 (2012) on the removal of Crystal Red, an anionic dye. Fig13 shows the adsorption of the dye;  
843 after only 15min, 97% of the dye is removed when starting from a solution with a  
844 concentration of  $100\text{ mg}\cdot\text{L}^{-1}$ . Moreover, LDH can be regenerated and cycled several times.  
845 Similar experiments were also performed by de Sá et al. (2013) with the Sunset Yellow FCF,  
846 a synthetic dye used to color food. The increase of the interlayer distance was observed,  
847 indicating that the adsorption takes place by simple ion exchange in this area. Magnetic  
848 materials can also be great sorbents towards organic dyes, as studied by Shan et al. (2014) by  
849 using magnetic  $Fe_3O_4/MgAl$  hydrotalcites to remove three different red dyes (reactive red,  
850 congo red, and acid red 1). The uptake equilibrium was reached after 30 min without  
851 significant impact on the solution pH. The different results reported all along this review show  
852 that the morphology of the LDHs has a great impact on the specific surface area and plays a

853 role on the adsorption capacity. A recent study performed by Li et al. (2016) focused on the  
854 adsorption of congo red by MgAl hydrotalcite. The specific surface area increased from 24.74  
855 to 165.07 m<sup>2</sup>.g<sup>-1</sup> upon calcination of the parent hydrotalcite, due to the enhancement of the  
856 microporosity deriving from the dehydroxylation of the layers and the decomposition of  
857 carbonate anions. However, only a slight increase of the adsorption capacity (from 0.186 to  
858 0.206 mmol.g<sup>-1</sup>) was observed. Indeed, the adsorption mechanism implies the anion exchange  
859 in the interlayer space and the sorption on the external surface, while the internal surface  
860 related to microporosity is not involved in the process due to accessibility problems.

861 The adsorption of aqueous pollutants, inorganic (toxic heavy metals) and organic (dyes and  
862 heavy molecules), by LDHs and derived mixed oxides has been discussed. Due to the increase  
863 of industrial and agricultural activities, these dangerous and harmful compounds can be found  
864 in high concentrations and need to be removed from aqueous media. Their sorption by  
865 lamellar materials, more specifically LDHs, is one of the most investigated solutions. As the  
866 adsorption of these pollutants takes place in the interlayer space and on the external surfaces,  
867 LDHs and derived mixed oxides with large external specific surface area are required. The co-  
868 precipitation method is the most employed because of its ability to form a wide range of  
869 LDHs with high crystallinity and reactive surfaces, mainly by substituting magnesium and/or  
870 aluminum by other metallic cations in the structure at different molar ratios. According to  
871 Table 6, similar specific surface areas were obtained with the samples synthesized by co-  
872 precipitation either at low or high supersaturation conditions (between 5 and 230 m<sup>2</sup>.g<sup>-1</sup>).  
873 Other synthesis methods such as the ball milling (Mahmoud et al. 2017) or the ethanol-water  
874 mediated solvothermal method (Li et al. 2016) are also interesting alternatives to obtain  
875 materials with high surface areas (around 150 m<sup>2</sup>.g<sup>-1</sup>). Based on the existing literature, the  
876 adsorption of aqueous pollutants on LDHs and their derived materials reveals to be a  
877 promising alternative.

878

879 **2.2. Other applications**

880 **2.2.1. Hydrogen production**

881 The need of alternative energies to replace fossil fuels is growing since the last decade.  
882 Hydrogen is a clean energy vector that can be produced from several processes such as steam  
883 reforming, partial oxidation, or Sorption Enhanced Reaction Process (SERP) (Marquevich et  
884 al. 2001; He et al. 2009, 2010; Halabi et al. 2012a, b; Chanburanasiri et al. 2013; Cesar et al.  
885 2016; Homsı et al. 2017). Hydrogen production is carried out in presence of CO<sub>2</sub> adsorption  
886 processes (as reported in the section “2.1.1 CO<sub>2</sub> adsorption – Capture and storage”). Sikander  
887 et al. (2017) reported in a review article the different hydrogen production processes carried  
888 out in the presence of hydrotalcite-base catalysts. The feedstock is generally constituted of  
889 light hydrocarbons such as ethanol, methanol or methane, even if biomass is a promising  
890 environment-friendly hydrogen source being highly available worldwide, relatively cheap and  
891 renewable (He et al. 2009, 2010; Contreras et al. 2014; Cesar et al. 2016; Zardin and Perez-  
892 Lopez 2017; García-Sancho et al. 2018; Sikander et al. 2018). The hydrogen production  
893 reactions are reported in the following equations (de Souza et al. 2012):

894 (1)  $C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$  in presence of ethanol in water,

895 (2)  $C_2H_5OH \rightarrow CH_3CHO + H_2$

896 (3)  $CH_3CHO \rightarrow CH_4 + CO$  by decomposition of ethanol and the further  
897 decomposition of acetaldehyde,

898 (4)  $CH_4 + H_2O \rightarrow CO + 3H_2$  in presence of methane in water,

899 (5)  $CH_4 + CO_2 \rightarrow 2CO + 2H_2$  in presence of methane in carbon dioxide.

900 The drawback in using hydrotalcite-derived catalysts for these processes is the high  
901 operating temperature needed (up to 900°C) to calcine the layered materials prior to the  
902 catalytic reaction. Moreover, the formation of carbon monoxide can lead to the formation of

903 carbonaceous materials (also named coke) that brings to the progressive deactivation of the  
904 active sites, as shown by de Souza et al. (2012) in the Boudouard reaction:  $2\text{CO} \rightarrow \text{CO}_2 +$   
905  $\text{C}_{(s)}$ . The synthesis conditions of the LDHs and related mixed oxides discussed in this part are  
906 summarized in Table 7.

907

908 The first experiments using LDHs to produce hydrogen were performed, in the last decade,  
909 by steam reforming. Markevich et al. (2001) studied the feasibility with sunflower oil, as  
910 feedstock, and Ni/Al mixed oxides derived from calcined LDHs, as catalyst. More recently,  
911 steam reforming was studied in the presence of hydrocarbons such as ethanol, methane or  
912 ethylene glycol. For each source, the key-point for process development is to identify the  
913 most efficient catalysts and synthesize it by varying the synthesis conditions or the chemical  
914 composition. Contreras et al. (2014) reported in a review article the various catalysts tested  
915 for hydrogen production by steam reforming. Ni-containing catalysts show very good  
916 catalytic activity for the conversion of ethanol and ethylene glycol, as shown by He et al.  
917 (2009, 2010) and Cesar et al. (2016), respectively. In the first case, the catalytic activity of  
918 Co-Ni catalysts decreased by increasing the nickel content. In presence of ethylene glycol,  
919 Cesar et al. (2016) showed that Pt-containing catalysts are the most active and selective.  
920 Finally, a complete study on the steam reforming process, carried out with methane as  
921 feedstock, has been reported by Halabi et al. (2012a, b), using calcined  $\text{K}_2\text{CO}_3$ -promoted  
922 Mg/Al hydrotalcite with in-situ  $\text{CO}_2$  capture. A similar study has been performed by  
923 Chanburanasiri et al. (2013) by comparing the impact of different commercial  $\text{K}_2\text{CO}_3$  on the  
924 sorption efficiency and  $\text{H}_2$  production. The co-precipitation method revealed to be the most  
925 adapted for the easy substitution of the cations in the structure. In some syntheses, co-  
926 precipitation was performed in the presence of urea in order to improve the crystal size and  
927 the number of active sites.

928 Methane decomposition is the second process largely studied for hydrogen production.  
929 Methane is firstly adsorbed on the surface of the catalysts and then decomposed on the active  
930 sites. Graphite-like structure or coke can accumulate on the active sites and block them,  
931 leading to a progressive deactivation of the catalyst. The presence of transition metals (Ni,  
932 Co) in the catalyst structure positively contributes to methane decomposition at low  
933 temperatures and with high yields. By varying the Cu/Al molar ratios (maintaining fixed Ni  
934 content) of calcined Ni/Cu/Al hydrotalcites, Ashok et al. (2008) identified the ideal  
935 composition (Ni/Cu/Al=60/25/15) to obtain the highest hydrogen yield. The amount of Ni in  
936 Ni/Mg/Al hydrotalcites can also be modulated; García-Sancho et al. (2017) investigated the  
937 influence of the nickel content on hydrogen production. Fig14. shows the methane conversion  
938 and the hydrogen production in the presence of hydrotalcites of various nickel content during  
939 temperature-programmed tests. 55% of methane conversion with 100% hydrogen selectivity  
940 was measured on a catalyst containing 46%<sub>at</sub> of nickel in the structure. The conversion was  
941 not improved by increasing the nickel content, due to the presence of inactive isolated Ni  
942 particles among the spinel phases. One year later, the same team (García-Sancho et al. 2018)  
943 compared the impact of adding nickel during the synthesis of hydrotalcites prior to the  
944 calcination and to form bulk Ni-mixed oxides, or after the calcination of the hydrotalcites (to  
945 produce Ni-supported mixed oxides). The two kind of catalysts show similar activities, and  
946 only slight differences in the reduction temperatures of the catalysts were observed. The  
947 impact of the calcination temperature was studied by Sikander et al. (2018) on Mg/Ni/Al  
948 hydrotalcites with different nickel content. The sample containing 40%<sub>at</sub> nickel showed the  
949 best performances after calcination at 500 and 750°C. The presence of spinel-like structures  
950 on the catalyst surface favors the diffusion of the deposited carbon, enhancing the overall  
951 catalytic activity.

952

953 Hydrogen can be produced by various processes, such as steam reforming and methane  
954 decomposition. Highly active and selective catalysts exist and are listed in Table 8. The  
955 possibility to tune the catalysts composition is fundamental to form mixed oxides with high  
956 catalytic activity. Most of the studies discussed in this section are focused on the co-  
957 precipitation method for the possibility of operating structural substitutions, particularly to  
958 add nickel cations in the LDH structure. Table 7 also shows the interest in using co-  
959 precipitated LDHs instead of commercial samples; the specific surface areas of the  
960 synthesized samples is higher than that of the commercial ones (between 69 and 156 m<sup>2</sup>.g<sup>-1</sup>  
961 instead of 15-104 in the commercial hydrotalcites). Urea is also introduced during preparation  
962 in order to obtain a high number of active sites and increase the size of the platelets.  
963 Moreover, the hydrogen production can be combined with CO<sub>2</sub> adsorption with interesting  
964 results. Combining CO<sub>2</sub> capture and H<sub>2</sub> formation in the same process is promising for future  
965 industrial applications.

966

#### 967 2.2.2.5-Hydroxymethylfurfural formation

968 Thanks to its natural abundance, biomass is a promising sustainable feedstock:  
969 carbohydrates are the largest natural carbon source constituting up to 75% of the annual  
970 biomass production, with promising applications in chemistry, food, paper, and  
971 pharmaceutical industries (Rosatella et al. 2011; Zakrzewska et al. 2011). Carbohydrates are  
972 rich in oxygen and can be easily reduced and dehydrated into a large spectrum of chemicals  
973 such as 5-Hydroxymethylfurfural (5-HMF) or levulinic acid. The US Department of Energy  
974 listed 5-HMF among the top 10 value-added chemicals; it is generally used as an intermediate  
975 to synthesize a wide range of chemicals nowadays derived from petroleum. Unfortunately, 5-  
976 HMF is not extensively produced at industrial scale due to the high production cost (van  
977 Putten et al. 2013). Fructose and glucose conversion are well-documented reactions that occur



978 at relatively low temperature (below 150°C). These mild reaction conditions allow the use of  
979 clays, hybrids and other lamellar materials as catalysts. The dehydration of fructose leads to  
980 the formation of 5-Hydroxymethylfurfural (5-HMF), the main reaction product, and other by-  
981 products, such as levulinic acid and formic acid, that are formed by degradation of 5-HMF, as  
982 explained in Fig15. The catalysts used in this reaction must present a high specific surface  
983 area in order to maximize the catalytic surface and react with the fructose dissolved in the  
984 solvent (generally water). These requirements can be fulfilled by LDHs synthesized by the  
985 sol-gel method or any other method implying a hydrothermal treatment, and that present high  
986 specific surface areas and an improved thermal stability. The synthesis parameters of all the  
987 cited samples are reported in Table 9.

988

989 The main drawback in using clays, hybrids and other lamellar materials in catalytic  
990 reactions is their thermal stability. In typical natural clays, dehydration occurs below 200°C  
991 with the removal of interlayer and surface water, while irreversible dehydroxylation with  
992 formation of oxides starts already around 350°C, depending on the type of metallic cations in  
993 the starting material. Several catalytic reactions occur above 300°C, thus the majority of the  
994 studies performed with LDHs is based on mixed oxide catalysts obtained by their calcination.  
995 However, few experiments have been performed on modified clay minerals such as  
996 montmorillonite; thanks to their expandable layers and swelling properties, these minerals can  
997 be easily modified by ion-exchange and pillaring in order to modify their structural properties.  
998 Lourvanij and Rorrer (1994) studied the partial dehydration of glucose to organic acids on  
999 iron-, chromium-, aluminum-, and non-pillared montmorillonite. Their large pore size (higher  
1000 than 10Å) allows the diffusion of glucose molecules (equal to 8.6Å) in the interlayer space, as  
1001 demonstrated by the Fig16. Depending on the reaction path, coke formation, leading to their  
1002 progressive deactivation, has been observed. Further studies have been performed by Fang et

1003 al. (2014) with a commercial montmorillonite (K-10) to compare the impact of the reaction  
1004 solvent: dimethyl sulfoxide (DMSO) and butyl-3-methylimidazole chloride ([BMIM]Cl) were  
1005 used. The results are shown in Fig17. and point out the higher conversion of glucose in  
1006 presence of higher concentrations of [BMIM]Cl in DMSO. The efficient recycling of the  
1007 solvent (up to six times) without significant loss of the catalytic activity was also observed.

1008 Beside the well-known basicity of hydrotalcites, LDHs and related materials, only few  
1009 studies on the dehydration of fructose in 5-Hydroxymethylfurfural have been performed on  
1010 these materials. However, recent researches pointed out the promising application of these  
1011 materials in the transformation of biomass-derived monomers (Chheda and Dumesic 2007; Li  
1012 et al. 2011; Climent et al. 2014). Zeolites are widely employed for such applications, but  
1013 mixed oxides represent a great alternative thanks to their easy synthesis by sol-gel method or  
1014 by simple thermal treatment of LDHs and hydrotalcites.

1015 In the case of glucose catalysis, three different reactions can be expected: dehydration,  
1016 isomerization, and retro-aldol condensation. The first reaction generally allows to form HMF  
1017 and levulinic acid in the presence of acid catalysts, while the other reactions are favored in the  
1018 presence of basic materials to form fructose or lactic acid. The bifunctional acid-base  
1019 properties of Al-Zr mixed oxides bring to different reaction products: HMF and levulinic acid  
1020 are formed by dehydration on the acid sites, while lactic acid and fructose are obtained by  
1021 isomerization and retro-aldol condensation in the basic sites.

1022 As explained in this part, the catalytic formation of 5-HMF by dehydration of glucose with  
1023 the use of hydrotalcites or LDHs is not much documented, but the potential use of their  
1024 related mixed oxides shows interesting results that may be promising for future researches as  
1025 zeolite substitutes and needs further investigations. Even if the specific surface areas of the  
1026 LDHs reported in the Table 9 are similar to those of modified montmorillonites, the catalytic

1027 activity in this application is related to the surface acidity, limiting the potential use of LDHs.  
1028 Moreover, the sol-gel method or hydrothermal treatment can be easily performed to obtain  
1029 LDHs adapted to this application.

1030

1031

## 1032 **Conclusion**

1033 LDHs, hydrotalcites and their related materials gained huge interest in the last decades  
1034 thanks to their simple synthesis processes and numerous applications. Even if they are mainly  
1035 synthesized by co-precipitation or hydrothermal methods, the possibility to combine different  
1036 M(II) and M(III) cations and interlayer anions in their structure allows to tailor the chemical  
1037 composition, as well as their structural properties (surface areas, pore sizes, number of active  
1038 sites), making them potential catalysts in several industrial and environmental processes.  
1039 Moreover, their memory effect permits to reuse them many times, which is interesting at  
1040 industrial scales.

1041 In this review, the impact of synthesis methods on the structural and textural properties of  
1042 LDHs has been discussed in order to identify the most suitable synthesis process for a chosen  
1043 environmental application. The adsorption of pollutants (atmospheric and aqueous) and  
1044 hydrogen production are important environmental applications in which LDHs can find their  
1045 place. The key parameter for implementing the use of LDHs and derived materials is the  
1046 choice of the appropriate synthesis process. The adsorption of pollutants requires high amount  
1047 of basic sites and strong thermal stability that can be obtained using the co-precipitation  
1048 method to synthesize LDHs. On the other side, the formation of 5-HMF takes place on the  
1049 acid sites that can be potentially obtained by sol-gel or hydrothermal synthesis. Finally, the  
1050 intercalation, impregnation or addition of appropriate elements (metals) with uniform

1051 dispersion is important for hydrogen production to increase the catalytic activity of  
1052 hydrotalcites (Fig18.).

1053

#### 1054 **Acknowledgements**

1055 The authors acknowledge the French Ministry of High Education and Research for the  
1056 Ph.D.-student fellowship allowed to Dylan Chaillot.

1057

#### 1058 **Abbreviations**

1059 LDH, Layered Double Hydroxide; 5-HMF, 5-Hydroxymethylfurfural; VOCs, Volatile  
1060 Organic Compounds; TEPA, TeraEthylenePentAmine; SERP, Sorption Enhanced Reaction  
1061 Process; HPLC, High Performance Liquid Chromatography; NMR, Nuclear Magnetic  
1062 resonance; DMSO, DiMethyl SulfOxide.

1063

#### 1064 **References**

1065 Abelló S, Mitchell S, Santiago M, et al (2010) Perturbing the properties of layered double hydroxides  
1066 by continuous coprecipitation with short residence time. *J Mater Chem* 20:5878.  
1067 <https://doi.org/10.1039/c0jm00088d>

1068 Adachi-Pagano M, Forano C, Besse J-P (2003) Synthesis of Al-rich hydrotalcite-like compounds by  
1069 using the urea hydrolysis reaction—control of size and morphology. *J Mater Chem* 13:1988–  
1070 1993. <https://doi.org/10.1039/B302747N>

1071 Aguilera DA, Perez A, Molina R, Moreno S (2011) Cu–Mn and Co–Mn catalysts synthesized from  
1072 hydrotalcites and their use in the oxidation of VOCs. *Appl Catal B Environ* 104:144–150.  
1073 <https://doi.org/10.1016/j.apcatb.2011.02.019>

1074 Ahmed IM, Gasser MS (2012) Adsorption study of anionic reactive dye from aqueous solution to Mg–  
1075 Fe–CO<sub>3</sub> layered double hydroxide (LDH). *Appl Surf Sci* 259:650–656.  
1076 <https://doi.org/10.1016/j.apsusc.2012.07.092>

1077 Albuquerque DWS, Costa ES, de Miranda JL, et al (2016) Evaluation of the Behavior of Hydrotalcite  
1078 Like-Materials for CO<sub>2</sub> Capture. *Appl Mech Mater* 830:3–10.  
1079 <https://doi.org/10.4028/www.scientific.net/AMM.830.3>

- 1080 Ali I (2012) New Generation Adsorbents for Water Treatment. *Chem Rev* 112:5073–5091.  
1081 <https://doi.org/10.1021/cr300133d>
- 1082 Alila S, Aloulou F, Thielemans W, Boufi S (2011) Sorption potential of modified nanocrystals for the  
1083 removal of aromatic organic pollutant from aqueous solution. *Ind Crops Prod* 33:350–357.  
1084 <https://doi.org/10.1016/j.indcrop.2010.11.010>
- 1085 Aramendía M (2002) Comparative Study of Mg/M(III) (M=Al, Ga, In) Layered Double Hydroxides  
1086 Obtained by Coprecipitation and the Sol–Gel Method. *J Solid State Chem* 168:156–161.  
1087 <https://doi.org/10.1006/jssc.2002.9655>
- 1088 Ashok J, Subrahmanyam M, Venugopal A (2008) Hydrotalcite structure derived Ni–Cu–Al catalysts for  
1089 the production of H<sub>2</sub> by CH<sub>4</sub> decomposition. *Int J Hydrog Energy* 33:2704–2713.  
1090 <https://doi.org/10.1016/j.ijhydene.2008.03.028>
- 1091 Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN (2013) The effects of catalysts in biodiesel  
1092 production: A review. *J Ind Eng Chem* 19:14–26. <https://doi.org/10.1016/j.jiec.2012.07.009>
- 1093 Atribak I, Azambre B, Bueno López A, García-García A (2009) Effect of NO<sub>x</sub> adsorption/desorption  
1094 over ceria-zirconia catalysts on the catalytic combustion of model soot. *Appl Catal B Environ*  
1095 92:126–137. <https://doi.org/10.1016/j.apcatb.2009.07.015>
- 1096 Bahranowski K, Bielanska E, Janik R, et al (1999) LDH-derived catalysts for complete oxidation of  
1097 volatile organic compounds. *Clay Miner* 34:67–77
- 1098 Balsamo N, Mendieta S, Oliva M, et al (2012) Synthesis and Characterization of Metal Mixed Oxides  
1099 from Layered Double Hydroxides. *Procedia Mater Sci* 1:506–513.  
1100 <https://doi.org/10.1016/j.mspro.2012.06.068>
- 1101 Bankauskaite A, Baltakys K (2011) The hydrothermal synthesis of hydrotalcite by using different  
1102 partially soluble and insoluble in water manganese and aluminium components. *Sci Sinter*  
1103 43:261–275. <https://doi.org/10.2298/SOS1103261B>
- 1104 Barrera-Díaz CE, Lugo-Lugo V, Bilyeu B (2012) A review of chemical, electrochemical and biological  
1105 methods for aqueous Cr(VI) reduction. *J Hazard Mater* 223–224:1–12.  
1106 <https://doi.org/10.1016/j.jhazmat.2012.04.054>
- 1107 Bedin KC, Martins AC, Cazetta AL, et al (2016) KOH-activated carbon prepared from sucrose spherical  
1108 carbon: Adsorption equilibrium, kinetic and thermodynamic studies for Methylene Blue  
1109 removal. *Chem Eng J* 286:476–484. <https://doi.org/10.1016/j.cej.2015.10.099>
- 1110 Beita-Sandí W, Ersan MS, Uzun H, Karanfil T (2016) Removal of N-nitrosodimethylamine precursors  
1111 with powdered activated carbon adsorption. *Water Res* 88:711–718.  
1112 <https://doi.org/10.1016/j.watres.2015.10.062>
- 1113 Benito P, Herrero M, Barriga C, et al (2008) Microwave-Assisted Homogeneous Precipitation of  
1114 Hydrotalcites by Urea Hydrolysis. *Inorg Chem* 47:5453–5463.  
1115 <https://doi.org/10.1021/ic7023023>
- 1116 Benito P, Labajos FM, Rives V (2006) Uniform Fast Growth of Hydrotalcite-like Compounds. *Cryst*  
1117 *Growth Des* 6:1961–1966. <https://doi.org/10.1021/cg0506222>

- 1118 Berber MR, Hafez IH, Minagawa K, et al (2013) Uniform nanoparticles of hydrotalcite-like materials  
1119 and their textural properties at optimized conditions of urea hydrothermal treatment. *J Mol*  
1120 *Struct* 1033:104–112. <https://doi.org/10.1016/j.molstruc.2012.08.028>
- 1121 Bhatta LKG, Subramanyam S, Chengala MD, et al (2015) Enhancement in CO<sub>2</sub> Adsorption on  
1122 Hydrotalcite-based Material by Novel Carbon Support Combined with K<sub>2</sub>CO<sub>3</sub> Impregnation.  
1123 *Ind Eng Chem Res* 54:10876–10884. <https://doi.org/10.1021/acs.iecr.5b02020>
- 1124 Bian L, Wang W, Xia R, Li Z (2016) Ni-based catalyst derived from Ni/Al hydrotalcite-like compounds  
1125 by the urea hydrolysis method for CO methanation. *RSC Adv* 6:677–686.  
1126 <https://doi.org/10.1039/C5RA19748A>
- 1127 Bish DL (1980) Anion-exchange in takovite : applications to other hydroxide minerals. *Bull*  
1128 *Minéralogie* 103:170–175. <https://doi.org/10.3406/bulmi.1980.7392>
- 1129 Bolognini M, Cavani F, Scagliarini D, et al (2003) Mg/Al mixed oxides prepared by coprecipitation and  
1130 sol–gel routes: a comparison of their physico-chemical features and performances in m-  
1131 cresol methylation. *Microporous Mesoporous Mater* 66:77–89.  
1132 <https://doi.org/10.1016/j.micromeso.2003.09.010>
- 1133 Bontchev RP, Liu S, Krumhansl JL, et al (2003) Synthesis, Characterization, and Ion Exchange  
1134 Properties of Hydrotalcite Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>(A)<sub>x</sub>(A')<sub>2-x</sub>·4H<sub>2</sub>O (A, A' = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>,  
1135 2 ≥ x ≥ 0) Derivatives. *Chem Mater* 15:3669–3675. <https://doi.org/10.1021/cm034231r>
- 1136 Breen JP, Burch R, Fontaine-Gautrelet C, et al (2008) Insight into the key aspects of the regeneration  
1137 process in the NO<sub>x</sub> storage reduction (NSR) reaction probed using fast transient kinetics  
1138 coupled with isotopically labelled <sup>15</sup>N<sub>2</sub> over Pt and Rh-containing Ba/Al<sub>2</sub>O<sub>3</sub> catalysts. *Appl*  
1139 *Catal B Environ* 81:150–159. <https://doi.org/10.1016/j.apcatb.2007.12.016>
- 1140 Budhysutanto WN, Kramer HJM, van Agterveld D, et al (2010) Pre-treatment of raw materials for the  
1141 hydrothermal synthesis of hydrotalcite-like compounds. *Chem Eng Res Des* 88:1445–1449.  
1142 <https://doi.org/10.1016/j.cherd.2009.10.010>
- 1143 Cantú M, López-Salinas E, Valente JS, Montiel R (2005) SO<sub>x</sub> Removal by Calcined MgAlFe  
1144 Hydrotalcite-like Materials: Effect of the Chemical Composition and the Cerium Incorporation  
1145 Method. *Environ Sci Technol* 39:9715–9720. <https://doi.org/10.1021/es051305m>
- 1146 Carpentier J, Lamonier JF, Siffert S, et al (2002) Characterisation of Mg/Al hydrotalcite with interlayer  
1147 palladium complex for catalytic oxidation of toluene. *Appl Catal Gen* 234:91–101.  
1148 [https://doi.org/10.1016/S0926-860X\(02\)00201-6](https://doi.org/10.1016/S0926-860X(02)00201-6)
- 1149 Castoldi L, Matarrese R, Lietti L, Forzatti P (2006) Simultaneous removal of NO<sub>x</sub> and soot on Pt–  
1150 Ba/Al<sub>2</sub>O<sub>3</sub> NSR catalysts. *Appl Catal B Environ* 64:25–34.  
1151 <https://doi.org/10.1016/j.apcatb.2005.10.015>
- 1152 Cesar DV, Santori GF, Pompeo F, et al (2016) Hydrogen production from ethylene glycol reforming  
1153 catalyzed by Ni and Ni–Pt hydrotalcite-derived catalysts. *Int J Hydrog Energy* 41:22000–  
1154 22008. <https://doi.org/10.1016/j.ijhydene.2016.07.168>
- 1155 Chanburanasiri N, Ribeiro AM, Rodrigues AE, et al (2013) Simulation of Methane Steam Reforming  
1156 Enhanced by *in Situ* CO<sub>2</sub> Sorption Using K<sub>2</sub>CO<sub>3</sub>-Promoted Hydrotalcites for H<sub>2</sub> Production.  
1157 *Energy Fuels* 27:4457–4470. <https://doi.org/10.1021/ef302043e>

- 1158 Chaparala SV, Raj A, Chung SH (2015) Reaction Mechanism for the Formation of Nitrogen Oxides (NO  
1159 x ) During Coke Oxidation in Fluidized Catalytic Cracking Units. *Combust Sci Technol*  
1160 187:1683–1704. <https://doi.org/10.1080/00102202.2015.1059328>
- 1161 Cheng H, Chen G, Wang S, et al (2004) NOx storage-reduction over Pt/Mg-Al-O catalysts with  
1162 different Mg/Al atomic ratios. *Korean J Chem Eng* 21:595–600.  
1163 <https://doi.org/10.1007/BF02705493>
- 1164 Cheng Q, Wang C, Doudrick K, Chan CK (2015) Hexavalent chromium removal using metal oxide  
1165 photocatalysts. *Appl Catal B Environ* 176–177:740–748.  
1166 <https://doi.org/10.1016/j.apcatb.2015.04.047>
- 1167 Chheda JN, Dumesic JA (2007) An overview of dehydration, aldol-condensation and hydrogenation  
1168 processes for production of liquid alkanes from biomass-derived carbohydrates. *Catal Today*  
1169 123:59–70. <https://doi.org/10.1016/j.cattod.2006.12.006>
- 1170 Chmielarz L, Piwowarska Z, Rutkowska M, et al (2012) Total oxidation of selected mono-carbon VOCs  
1171 over hydrotalcite originated metal oxide catalysts. *Catal Commun* 17:118–125.  
1172 <https://doi.org/10.1016/j.catcom.2011.10.030>
- 1173 Chuang YH, Tzou YM, Wang MK, et al (2008) Removal of 2-Chlorophenol from Aqueous Solution by  
1174 Mg/Al Layered Double Hydroxide (LDH) and Modified LDH. *Ind Eng Chem Res* 47:3813–3819.  
1175 <https://doi.org/10.1021/ie071508e>
- 1176 Climent M (2004) Increasing the basicity and catalytic activity of hydrotalcites by different synthesis  
1177 procedures. *J Catal* 225:316–326. <https://doi.org/10.1016/j.jcat.2004.04.027>
- 1178 Climent MJ, Corma A, Iborra S (2014) Conversion of biomass platform molecules into fuel additives  
1179 and liquid hydrocarbon fuels. *Green Chem* 16:516. <https://doi.org/10.1039/c3gc41492b>
- 1180 Climent MJ, Corma A, Iborra S, Velty A (2004) Activated hydrotalcites as catalysts for the synthesis of  
1181 chalcones of pharmaceutical interest. *J Catal* 221:474–482.  
1182 <https://doi.org/10.1016/j.jcat.2003.09.012>
- 1183 Coenen K, Gallucci F, Cobden P, et al (2017a) Chemisorption of H<sub>2</sub>O and CO<sub>2</sub> on Hydrotalcites for  
1184 Sorption-enhanced Water-gas-Shift Processes. *Energy Procedia* 114:2228–2242.  
1185 <https://doi.org/10.1016/j.egypro.2017.03.1360>
- 1186 Coenen K, Gallucci F, Mezari B, et al (2018) An in-situ IR study on the adsorption of CO<sub>2</sub> and H<sub>2</sub>O on  
1187 hydrotalcites. *J CO<sub>2</sub> Util* 24:228–239. <https://doi.org/10.1016/j.jcou.2018.01.008>
- 1188 Coenen K, Gallucci F, Pio G, et al (2017b) On the influence of steam on the CO<sub>2</sub> chemisorption  
1189 capacity of a hydrotalcite-based adsorbent for SEWGS applications. *Chem Eng J* 314:554–569.  
1190 <https://doi.org/10.1016/j.cej.2016.12.013>
- 1191 Colonna S, Bastianini M, Sisani M, Fina A (2018) CO<sub>2</sub> adsorption and desorption properties of  
1192 calcined layered double hydroxides: Effect of metal composition on the LDH structure. *J*  
1193 *Therm Anal Calorim* 133:869–879. <https://doi.org/10.1007/s10973-018-7152-8>
- 1194 Contreras JL, Salmones J, Colín-Luna JA, et al (2014) Catalysts for H<sub>2</sub> production using the ethanol  
1195 steam reforming (a review). *Int J Hydrog Energy* 39:18835–18853.  
1196 <https://doi.org/10.1016/j.ijhydene.2014.08.072>

- 1197 Corma A, Fornés V, Rey F (1994) Hydrotalcites as Base Catalysts: Influence of the Chemical  
1198 Composition and Synthesis Conditions on the Dehydrogenation of Isopropanol. *J Catal*  
1199 148:205–212
- 1200 Corma A, Palomares AE, Rey F, Márquez F (1997) Simultaneous Catalytic Removal of SO<sub>x</sub> and NO<sub>x</sub> with  
1201 Hydrotalcite-Derived Mixed Oxides Containing Copper, and Their Possibilities to Be Used in  
1202 FCC Units. *J Catal* 170:140–149. <https://doi.org/10.1006/jcat.1997.1750>
- 1203 Costantino U, Marmottini F, Nocchetti M, Vivani R (1998) New Synthetic Routes to Hydrotalcite-Like  
1204 Compounds – Characterisation and Properties of the Obtained Materials. *Eur J Inorg Chem*  
1205 1998:1439–1446. [https://doi.org/10.1002/\(SICI\)1099-0682\(199810\)1998:10<1439::AID-  
1206 EJIC1439>3.0.CO;2-1](https://doi.org/10.1002/(SICI)1099-0682(199810)1998:10<1439::AID-EJIC1439>3.0.CO;2-1)
- 1207 Cui, Ma, Wang, et al (2019) High Performance of Mn-Doped MgAlO<sub>x</sub> Mixed Oxides for Low  
1208 Temperature NO<sub>x</sub> Storage and Release. *Catalysts* 9:677.  
1209 <https://doi.org/10.3390/catal9080677>
- 1210 Dadwhal M, Kim TW, Sahimi M, Tsotsis TT (2008) Study of CO<sub>2</sub> Diffusion and Adsorption on Calcined  
1211 Layered Double Hydroxides: The Effect of Particle Size. *Ind Eng Chem Res* 47:6150–6157.  
1212 <https://doi.org/10.1021/ie701701d>
- 1213 Dantas TCM, Junior VJF, Santos APB dos, et al (2015) CO<sub>2</sub> Adsorption on Modified Mg–Al-Layered  
1214 Double Hydroxides. *Adsorpt Sci Technol* 33:165–173. [https://doi.org/10.1260/0263-  
1215 6174.33.2.165](https://doi.org/10.1260/0263-6174.33.2.165)
- 1216 de Sá FP, Cunha BN, Nunes LM (2013) Effect of pH on the adsorption of Sunset Yellow FCF food dye  
1217 into a layered double hydroxide (CaAl-LDH-NO<sub>3</sub>). *Chem Eng J* 215–216:122–127.  
1218 <https://doi.org/10.1016/j.cej.2012.11.024>
- 1219 de Souza G, Ávila VC, Marcílio NR, Perez-Lopez OW (2012) Synthesis Gas Production by Steam  
1220 Reforming of Ethanol over M-Ni-Al Hydrotalcite-type Catalysts; M=Mg, Zn, Mo, Co. *Procedia*  
1221 *Eng* 42:1805–1815. <https://doi.org/10.1016/j.proeng.2012.07.575>
- 1222 Dou Y, Zhou S, Oldani C, et al (2018) 5-Hydroxymethylfurfural production from dehydration of  
1223 fructose catalyzed by Aquivion@silica solid acid. *Fuel* 214:45–54.  
1224 <https://doi.org/10.1016/j.fuel.2017.10.124>
- 1225 Dula R, Janik R, Machej T, et al (2007) Mn-containing catalytic materials for the total combustion of  
1226 toluene: The role of Mn localisation in the structure of LDH precursor. *Catal Today* 119:327–  
1227 331. <https://doi.org/10.1016/j.cattod.2006.08.060>
- 1228 El Rouby WMA, El-Dek SI, Goher ME, Noaemy SG (2018) Efficient water decontamination using  
1229 layered double hydroxide beads nanocomposites. *Environ Sci Pollut Res*.  
1230 <https://doi.org/10.1007/s11356-018-3257-7>
- 1231 El-Sayed M, Eshaq Gh, ElMetwally AE (2016) Adsorption of heavy metals from aqueous solutions by  
1232 Mg–Al–Zn mingled oxides adsorbent. *Water Sci Technol* 74:1644–1657.  
1233 <https://doi.org/10.2166/wst.2016.329>
- 1234 Fang Z, Liu B, Luo J, et al (2014) Efficient conversion of carbohydrates into 5-hydroxymethylfurfural  
1235 catalyzed by the chromium-exchanged montmorillonite K-10 clay. *Biomass Bioenergy*  
1236 60:171–177. <https://doi.org/10.1016/j.biombioe.2013.12.002>



- 1237 Forzatti P, Nova I, Tronconi E (2010) New “Enhanced NH<sub>3</sub>-SCR” Reaction for NO<sub>x</sub> Emission Control.  
1238 Ind Eng Chem Res 49:10386–10391. <https://doi.org/10.1021/ie100600v>
- 1239 Fosso-Kankeu E, Mulaba-Bafubiandi AF, Mamba BB, et al (2010) A comprehensive study of physical  
1240 and physiological parameters that affect bio-sorption of metal pollutants from aqueous  
1241 solutions. Phys Chem Earth Parts ABC 35:672–678.  
1242 <https://doi.org/10.1016/j.pce.2010.07.008>
- 1243 Gao C, Shi J-W, Fan Z, et al (2018) “Fast SCR” reaction over Sm-modified MnO<sub>x</sub>-TiO<sub>2</sub> for promoting  
1244 reduction of NO<sub>x</sub> with NH<sub>3</sub>. Appl Catal Gen 564:102–112.  
1245 <https://doi.org/10.1016/j.apcata.2018.07.017>
- 1246 Gao Y, Zhang Z, Wu J, et al (2013) Comprehensive investigation of CO<sub>2</sub> adsorption on Mg–Al–CO<sub>3</sub>  
1247 LDH-derived mixed metal oxides. J Mater Chem A 1:12782.  
1248 <https://doi.org/10.1039/c3ta13039h>
- 1249 García-Sancho C, Guil-López R, Pascual L, et al (2017) Optimization of nickel loading of mixed oxide  
1250 catalyst ex-hydrotalcite for H<sub>2</sub> production by methane decomposition. Appl Catal Gen  
1251 548:71–82. <https://doi.org/10.1016/j.apcata.2017.07.038>
- 1252 García-Sancho C, Guil-López R, Sebastián-López A, et al (2018) Hydrogen production by methane  
1253 decomposition: A comparative study of supported and bulk ex-hydrotalcite mixed oxide  
1254 catalysts with Ni, Mg and Al. Int J Hydrog Energy 43:9607–9621.  
1255 <https://doi.org/10.1016/j.ijhydene.2018.04.021>
- 1256 Gastuche MC, Brown G, Mortland MM (1967) Mixed Magnesium-Aluminium Hydroxides I.  
1257 Preparation and Characterization of Compounds Formed in Dialysed Systems. Clay Miner  
1258 7:177–192
- 1259 Gennequin C, Barakat T, Tidahy HL, et al (2010a) Use and observation of the hydrotalcite “memory  
1260 effect” for VOC oxidation. Catal Today 157:191–197.  
1261 <https://doi.org/10.1016/j.cattod.2010.03.012>
- 1262 Gennequin C, Kouassi S, Tidahy L, et al (2010b) Co–Mg–Al oxides issued of hydrotalcite precursors for  
1263 total oxidation of volatile organic compounds. Identification and toxicological impact of the  
1264 by-products. Comptes Rendus Chim 13:494–501. <https://doi.org/10.1016/j.crci.2010.01.001>
- 1265 Gennequin C, Siffert S, Cousin R, Aboukais A (2009) Co–Mg–Al Hydrotalcite Precursors for Catalytic  
1266 Total Oxidation of Volatile Organic Compounds. Top Catal 52:482–491.  
1267 <https://doi.org/10.1007/s11244-009-9183-7>
- 1268 Gevers BR, Naseem S, Leuteritz A, Labuschagné FJWJ (2019) Comparison of nano-structured  
1269 transition metal modified tri-metal MgAl-LDHs (M = Fe, Zn, Cu, Ni, Co) prepared using co-  
1270 precipitation. RSC Adv 9:28262–28275. <https://doi.org/10.1039/C9RA05452A>
- 1271 Gramigni F, Selleri T, Nova I, Tronconi E (2019) Catalyst systems for selective catalytic reduction + NO<sub>x</sub>  
1272 trapping: from fundamental understanding of the standard SCR reaction to practical  
1273 applications for lean exhaust after-treatment. React Chem Eng 4:1165–1178.  
1274 <https://doi.org/10.1039/C9RE00012G>
- 1275 Gunugunuri K, Roberts CA (2019) Direct NO<sub>x</sub> decomposition catalyst with improved activity and  
1276 selectivity

- 1277 Gunugunuri KR, Peck TC, Ling C, Jia H (2018) Catalyst for direct nox decomposition and a method of  
1278 forming and using the catalyst
- 1279 Guo X, Wu Z, He M (2009) Removal of antimony(V) and antimony(III) from drinking water by  
1280 coagulation–flocculation–sedimentation (CFS). *Water Res* 43:4327–4335.  
1281 <https://doi.org/10.1016/j.watres.2009.06.033>
- 1282 Guo Z, Chen Y, Lu NL (2018) Multifunctional Nanocomposites for Energy and Environmental  
1283 Applications. John Wiley & Sons
- 1284 Halabi MH, de Croon MHJM, van der Schaaf J, et al (2012a) High capacity potassium-promoted  
1285 hydrotalcite for CO<sub>2</sub> capture in H<sub>2</sub> production. *Int J Hydrog Energy* 37:4516–4525.  
1286 <https://doi.org/10.1016/j.ijhydene.2011.12.003>
- 1287 Halabi MH, de Croon MHJM, van der Schaaf J, et al (2012b) A novel catalyst–sorbent system for an  
1288 efficient H<sub>2</sub> production with in-situ CO<sub>2</sub> capture. *Int J Hydrog Energy* 37:4987–4996.  
1289 <https://doi.org/10.1016/j.ijhydene.2011.12.025>
- 1290 He L, Berntsen H, Chen D (2010) Approaching Sustainable H<sub>2</sub> Production: Sorption Enhanced Steam  
1291 Reforming of Ethanol<sup>†</sup>. *J Phys Chem A* 114:3834–3844. <https://doi.org/10.1021/jp906146y>
- 1292 He L, Berntsen H, Ochoa-Fernández E, et al (2009) Co–Ni Catalysts Derived from Hydrotalcite-Like  
1293 Materials for Hydrogen Production by Ethanol Steam Reforming. *Top Catal* 52:206–217.  
1294 <https://doi.org/10.1007/s11244-008-9157-1>
- 1295 Helwani Z, Othman MR, Aziz N, et al (2009) Technologies for production of biodiesel focusing on  
1296 green catalytic techniques: A review. *Fuel Process Technol* 90:1502–1514.  
1297 <https://doi.org/10.1016/j.fuproc.2009.07.016>
- 1298 Hibino T, Ohya H (2009) Synthesis of crystalline layered double hydroxides: Precipitation by using  
1299 urea hydrolysis and subsequent hydrothermal reactions in aqueous solutions. *Appl Clay Sci*  
1300 45:123–132. <https://doi.org/10.1016/j.clay.2009.04.013>
- 1301 Homsy D, Rached JA, Aouad S, et al (2017) Steam reforming of ethanol for hydrogen production over  
1302 Cu/Co-Mg-Al-based catalysts prepared by hydrotalcite route. *Environ Sci Pollut Res* 24:9907–  
1303 9913. <https://doi.org/10.1007/s11356-016-7480-9>
- 1304 Imanaka N, Masui T (2012) Advances in direct NO<sub>x</sub> decomposition catalysts. *Appl Catal Gen* 431–  
1305 432:1–8. <https://doi.org/10.1016/j.apcata.2012.02.047>
- 1306 Inayat A, Klumpp M, Schwieger W (2011) The urea method for the direct synthesis of ZnAl layered  
1307 double hydroxides with nitrate as the interlayer anion. *Appl Clay Sci* 51:452–459.  
1308 <https://doi.org/10.1016/j.clay.2011.01.008>
- 1309 Ishihara S, Sahoo P, Deguchi K, et al (2013) Dynamic Breathing of CO<sub>2</sub> by Hydrotalcite. *J Am Chem*  
1310 *Soc* 135:18040–18043. <https://doi.org/10.1021/ja4099752>
- 1311 Iyi N, Matsumoto T, Kaneko Y, Kitamura K (2004) Deintercalation of Carbonate Ions from a  
1312 Hydrotalcite-Like Compound: Enhanced Decarbonation Using Acid–Salt Mixed Solution.  
1313 *Chem Mater* 16:2926–2932. <https://doi.org/10.1021/cm049579g>

- 1314 Jang HJ, Lee CH, Kim S, et al (2014) Hydrothermal Synthesis of  $K_2CO_3$ -Promoted Hydrotalcite from  
 1315 Hydroxide-Form Precursors for Novel High-Temperature  $CO_2$  Sorbent. ACS Appl Mater  
 1316 Interfaces 6:6914–6919. <https://doi.org/10.1021/am500720f>
- 1317 Jiang Y, Ling J, Xiao P, et al (2018) Simultaneous biogas purification and  $CO_2$  capture by vacuum swing  
 1318 adsorption using zeolite NaUSY. Chem Eng J 334:2593–2602.  
 1319 <https://doi.org/10.1016/j.cej.2017.11.090>
- 1320 Jitianu M, Soiu ML, Zaharescu M, et al (2000) Comparative Study of Sol-Gel and Coprecipitated Ni-Al  
 1321 Hydrotalcites. J Sol-Gel Sci Technol 19:453–457
- 1322 Kamal MS, Razzak SA, Hossain MM (2016) Catalytic oxidation of volatile organic compounds (VOCs) –  
 1323 A review. Atmos Environ 140:117–134. <https://doi.org/10.1016/j.atmosenv.2016.05.031>
- 1324 Kameda T, Tochinali M, Kumagai S, Yoshioka T (2019a) Simultaneous treatment of HCl– $SO_2$ – $NO_x$  gas  
 1325 with Mg–Al layered double hydroxide intercalated with  $CO_3^{2-}$  and its recycling process. Int J  
 1326 Environ Sci Technol. <https://doi.org/10.1007/s13762-019-02529-7>
- 1327 Kameda T, Tochinali M, Kumagai S, Yoshioka T (2020) Simultaneous treatment of HCl– $SO_2$ – $NO_x$  gas  
 1328 with Mg–Al layered double hydroxide intercalated with  $CO_3^{2-}$  and its recycling process. Int J  
 1329 Environ Sci Technol 17:1179–1184. <https://doi.org/10.1007/s13762-019-02529-7>
- 1330 Kameda T, Tochinali M, Kumagai S, Yoshioka T (2019b) Treatment of  $NO_x$  using recyclable  $CO_3^{2-}$ -  
 1331 intercalated Mg–Al layered double hydroxide. Atmospheric Pollut Res 10:1866–1872.  
 1332 <https://doi.org/10.1016/j.apr.2019.07.018>
- 1333 Kameda T, Uchiyama N, Yoshioka T (2011) Removal of HCl,  $SO_2$ , and NO by treatment of acid gas  
 1334 with Mg–Al oxide slurry. Chemosphere 82:587–591.  
 1335 <https://doi.org/10.1016/j.chemosphere.2010.11.020>
- 1336 Kannan S, Rives V, Knözinger H (2004) High-temperature transformations of Cu-rich hydrotalcites. J  
 1337 Solid State Chem 177:319–331. <https://doi.org/10.1016/j.jssc.2003.08.023>
- 1338 Kannan S, Velu S, Ramkumar V, Swamy CS (1995) Synthesis and physicochemical properties of cobalt  
 1339 aluminium hydrotalcites. J Mater Sci 30:1462–1468. <https://doi.org/10.1007/BF00375249>
- 1340 Karickhoff SW (1984) Organic Pollutant Sorption in Aquatic Systems. J Hydraul Eng 110:707–735.  
 1341 [https://doi.org/10.1061/\(ASCE\)0733-9429\(1984\)110:6\(707\)](https://doi.org/10.1061/(ASCE)0733-9429(1984)110:6(707))
- 1342 Klemkaite K, Prosycevas I, Taraskevicius R, et al (2011) Synthesis and characterization of layered  
 1343 double hydroxides with different cations (Mg, Co, Ni, Al), decomposition and reformation of  
 1344 mixed metal oxides to layered structures. Cent Eur J Chem 9:275–282.  
 1345 <https://doi.org/10.2478/s11532-011-0007-9>
- 1346 Klopogge JT, Hickey L, Frost RL (2004) The effects of synthesis pH and hydrothermal treatment on  
 1347 the formation of zinc aluminum hydrotalcites. J Solid State Chem 177:4047–4057.  
 1348 <https://doi.org/10.1016/j.jssc.2004.07.010>
- 1349 Klopogge JT, Hickey L, Trujillano R, et al (2006) Characterization of Intercalated Ni/Al Hydrotalcites  
 1350 Prepared by the Partial Decomposition of Urea. Cryst Growth Des 6:1533–1536.  
 1351 <https://doi.org/10.1021/cg0504612>

- 1352 Kovanda F, Grygar T, Dorničák V, et al (2005a) Thermal behaviour of Cu–Mg–Mn and Ni–Mg–Mn  
1353 layered double hydroxides and characterization of formed oxides. *Appl Clay Sci* 28:121–136.  
1354 <https://doi.org/10.1016/j.clay.2004.01.007>
- 1355 Kovanda F, Jirátová K (2011a) Supported layered double hydroxide-related mixed oxides and their  
1356 application in the total oxidation of volatile organic compounds. *Appl Clay Sci* 53:305–316.  
1357 <https://doi.org/10.1016/j.clay.2010.12.030>
- 1358 Kovanda F, Jirátová K (2011b) Supported mixed oxide catalysts for the total oxidation of volatile  
1359 organic compounds. *Catal Today* 176:110–115. <https://doi.org/10.1016/j.cattod.2011.02.002>
- 1360 Kovanda F, Koloušek D, Cílová Z, Hulínský V (2005b) Crystallization of synthetic hydrotalcite under  
1361 hydrothermal conditions. *Appl Clay Sci* 28:101–109.  
1362 <https://doi.org/10.1016/j.clay.2004.01.009>
- 1363 Koyuncu I (2002) Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing  
1364 vinylsulphone dyes: effects of feed concentration and cross flow velocity. *Desalination*  
1365 143:243–253. [https://doi.org/10.1016/S0011-9164\(02\)00263-1](https://doi.org/10.1016/S0011-9164(02)00263-1)
- 1366 Labuschagné FJWJ, Wiid A, Venter HP, et al (2018) Green synthesis of hydrotalcite from untreated  
1367 magnesium oxide and aluminum hydroxide. *Green Chem Lett Rev* 11:18–28.  
1368 <https://doi.org/10.1080/17518253.2018.1426791>
- 1369 Lau W-J, Ismail AF (2009) Polymeric nanofiltration membranes for textile dye wastewater treatment:  
1370 Preparation, performance evaluation, transport modelling, and fouling control — a review.  
1371 *Desalination* 245:321–348. <https://doi.org/10.1016/j.desal.2007.12.058>
- 1372 Lee G, Kang JY, Yan N, et al (2016) Simple preparation method for Mg–Al hydrotalcites as base  
1373 catalysts. *J Mol Catal Chem* 423:347–355. <https://doi.org/10.1016/j.molcata.2016.07.018>
- 1374 Lehmann M, Zouboulis AI, Matis KA (1999) Removal of metal ions from dilute aqueous solutions: A  
1375 comparative study of inorganic sorbent materials. *Chemosphere* 39:881–892.  
1376 [https://doi.org/10.1016/S0045-6535\(99\)00031-4](https://doi.org/10.1016/S0045-6535(99)00031-4)
- 1377 Leinonen H, Lehto J, Mäkelä A (1994) Purification of nickel and zinc from waste waters of metal-  
1378 plating plants by ion exchange. *React Polym* 23:221–228. [https://doi.org/10.1016/0923-1137\(94\)90024-8](https://doi.org/10.1016/0923-1137(94)90024-8)
- 1380 León M, Díaz E, Bennici S, et al (2010) Adsorption of CO<sub>2</sub> on Hydrotalcite-Derived Mixed Oxides:  
1381 Sorption Mechanisms and Consequences for Adsorption Irreversibility. *Ind Eng Chem Res*  
1382 49:3663–3671. <https://doi.org/10.1021/ie902072a>
- 1383 Li B, Zhang Y, Zhou X, et al (2016) Different dye removal mechanisms between monodispersed and  
1384 uniform hexagonal thin plate-like MgAl–CO<sub>3</sub>–LDH and its calcined product in efficient  
1385 removal of Congo red from water. *J Alloys Compd* 673:265–271.  
1386 <https://doi.org/10.1016/j.jallcom.2016.02.248>
- 1387 Li D, Wang L, Koike M, et al (2011) Steam reforming of tar from pyrolysis of biomass over Ni/Mg/Al  
1388 catalysts prepared from hydrotalcite-like precursors. *Appl Catal B Environ* 102:528–538.  
1389 <https://doi.org/10.1016/j.apcatb.2010.12.035>

- 1390 Li LD, Yu JJ, Hao ZP, Xu ZP (2007) Novel Ru–Mg–Al–O Catalyst Derived from Hydrotalcite-like  
 1391 Compound for NO Storage/Decomposition/Reduction. *J Phys Chem C* 111:10552–10559.  
 1392 <https://doi.org/10.1021/jp0678352>
- 1393 Li S, Guo Y, Xiao M, et al (2019a) Enhanced arsenate removal from aqueous solution by Mn-doped  
 1394 MgAl-layered double hydroxides. *Environ Sci Pollut Res* 26:12014–12024.  
 1395 <https://doi.org/10.1007/s11356-019-04667-4>
- 1396 Li X, Du Y, Guo X, et al (2019b) Synthesis of a Novel NiMnTi Mixed Metal Oxides from LDH Precursor  
 1397 and Its Catalytic Application for Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub>. *Catal Lett*  
 1398 149:456–464. <https://doi.org/10.1007/s10562-018-2626-7>
- 1399 Li Z, Chen F, Yuan L, et al (2012) Uranium(VI) adsorption on graphene oxide nanosheets from  
 1400 aqueous solutions. *Chem Eng J* 210:539–546. <https://doi.org/10.1016/j.cej.2012.09.030>
- 1401 Liao L, Zhao N, Xia Z (2012) Hydrothermal synthesis of Mg–Al layered double hydroxides (LDHs) from  
 1402 natural brucite and Al(OH)<sub>3</sub>. *Mater Res Bull* 47:3897–3901.  
 1403 <https://doi.org/10.1016/j.materresbull.2012.07.007>
- 1404 Lin Y, Wang X, Hao J, et al (2019) Preparation of CuZnAl hydrotalcite-like catalysts for AsH<sub>3</sub>  
 1405 abatement at low temperatures. *Catal Commun* 118:51–55.  
 1406 <https://doi.org/10.1016/j.catcom.2018.03.028>
- 1407 Lopez T, Bosch P, Asomoza M, et al (1997a) DTA-TGA and FTIR spectroscopies of sol-gel hydrotalcites:  
 1408 aluminum source effect on physicochemical properties. *Mater Lett* 31:311–316
- 1409 Lopez T, Bosch P, Ramos E, et al (1996) Synthesis and Characterization of Sol–Gel Hydrotalcites.  
 1410 Structure and Texture<sup>†</sup>. *Langmuir* 12:189–192. <https://doi.org/10.1021/la940703s>
- 1411 Lopez T, Ramos E, Bosch P, et al (1997b) DTA and TGA characterization of sol-gel hydrotalcites. *Mater*  
 1412 *Lett* 30:279–282. [https://doi.org/10.1016/S0167-577X\(96\)00214-5](https://doi.org/10.1016/S0167-577X(96)00214-5)
- 1413 Lourvanij K, Rorrer GL (1994) Dehydration of glucose to organic acids in microporous pillared clay  
 1414 catalysts. *Appl Catal Gen* 109:147–165. [https://doi.org/10.1016/0926-860X\(94\)85008-9](https://doi.org/10.1016/0926-860X(94)85008-9)
- 1415 Lukyanov DB, Sill G, d'Itri JL, Hall WK (1995) Comparison of Catalyzed and Homogeneous Reactions of  
 1416 Hydrocarbons for Selective Catalytic Reduction (SCR) of NO<sub>x</sub>. *J Catal* 153:265–274
- 1417 Lv L, He J, Wei M, et al (2006) Factors influencing the removal of fluoride from aqueous solution by  
 1418 calcined Mg–Al–CO<sub>3</sub> layered double hydroxides. *J Hazard Mater* 133:119–128.  
 1419 <https://doi.org/10.1016/j.jhazmat.2005.10.012>
- 1420 Mahmoud R, Moaty SA, Mohamed F, Farghali A (2017) Comparative Study of Single and Multiple  
 1421 Pollutants System Using Ti–Fe Chitosan LDH Adsorbent with High Performance in  
 1422 Wastewater Treatment. *J Chem Eng Data* 62:3703–3722.  
 1423 <https://doi.org/10.1021/acs.jced.7b00453>
- 1424 Mahzoul H, Brillhac JF, Gilot P (1999) Experimental and mechanistic study of NO<sub>x</sub> adsorption over  
 1425 NO<sub>x</sub> trap catalysts. *Appl Catal B Environ* 20:47–55. [https://doi.org/10.1016/S0926-3373\(98\)00093-9](https://doi.org/10.1016/S0926-3373(98)00093-9)  
 1426

- 1427 Mao G, Tamaura Y (1993) SYNTHESIS AND CO<sub>2</sub> ADSORPTION FEATURES OF A HYDROTALCITE-LIKE  
1428 COMPOUND OF THE Mg<sup>2+</sup>-Al<sup>3+</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> SYSTEM WITH HIGH LAYER-CHARGE DENSITY.  
1429 *Clays Clay Miner* 41:7
- 1430 Marquevich M, Medina F, Montan D (2001) Hydrogen production via steam reforming of sun<sup>-</sup>ower  
1431 oil over Ni/Al catalysts from hydrotalcite materials. *Catal Commun* 6
- 1432 Mathieu Y, Tzanis L, Soulard M, et al (2013) Adsorption of SO<sub>x</sub> by oxide materials: A review. *Fuel*  
1433 *Process Technol* 114:81–100. <https://doi.org/10.1016/j.fuproc.2013.03.019>
- 1434 Mazur LP, Pozdniakova TA, Mayer DA, et al (2016) Design of a fixed-bed ion-exchange process for the  
1435 treatment of rinse waters generated in the galvanization process using *Laminaria hyperborea*  
1436 as natural cation exchanger. *Water Res* 90:354–368.  
1437 <https://doi.org/10.1016/j.watres.2015.12.027>
- 1438 Megías-Sayago C, Bingre R, Huang L, et al (2019) CO<sub>2</sub> Adsorption Capacities in Zeolites and Layered  
1439 Double Hydroxide Materials. *Front Chem* 7:551. <https://doi.org/10.3389/fchem.2019.00551>
- 1440 Mikulová Z, Čuba P, Balabánová J, et al (2007) Calcined Ni–Al layered double hydroxide as a catalyst  
1441 for total oxidation of volatile organic compounds: Effect of precursor crystallinity. *Chem Pap*  
1442 61:. <https://doi.org/10.2478/s11696-007-0006-7>
- 1443 Milutinović-Nikolić A, Maksin D, Jović-Jovičić N, et al (2014) Removal of <sup>99</sup>Tc(VII) by organo-modified  
1444 bentonite. *Appl Clay Sci* 95:294–302. <https://doi.org/10.1016/j.clay.2014.04.027>
- 1445 Miyata S (1975) The Syntheses of Hydrotalcite-like Compounds and their Structures and Physico-  
1446 chemical Properties I. The Systems Mg<sup>2+</sup>-Al<sup>3+</sup>-NO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup>-Al<sup>3+</sup>-Cl<sup>-</sup>, Mg<sup>2+</sup>-Al<sup>3+</sup>-ClO<sub>4</sub><sup>-</sup>, Ni<sup>2+</sup>-  
1447 Al<sup>3+</sup>-Cl<sup>-</sup> and Zn<sup>2+</sup>-Al<sup>3+</sup>-Cl<sup>-</sup>. *Clays Clay Miner* 23:369–375
- 1448 Miyata S (1980) Physico-Chemical Properties of Synthetic Hydrotalcites in Relation to Composition.  
1449 *Clays Clay Miner* 28:50–56. <https://doi.org/10.1346/CCMN.1980.0280107>
- 1450 Montañez MK, Molina R, Moreno S (2014) Nickel catalysts obtained from hydrotalcites by  
1451 coprecipitation and urea hydrolysis for hydrogen production. *Int J Hydrog Energy* 39:8225–  
1452 8237. <https://doi.org/10.1016/j.ijhydene.2014.03.103>
- 1453 Moreira RFPM, Soares JL, Casarin GL, Rodrigues AE (2006) Adsorption of CO<sub>2</sub> on Hydrotalcite-like  
1454 Compounds in a Fixed Bed. *Sep Sci Technol* 41:341–357.  
1455 <https://doi.org/10.1080/01496390500496827>
- 1456 Mrad R, Cousin R, Saliba NA, et al (2015) Degradation of VOCs and NO<sub>x</sub> over Mg(Cu)–AlFe mixed  
1457 oxides derived from hydrotalcite-like compounds. *Comptes Rendus Chim* 18:351–357.  
1458 <https://doi.org/10.1016/j.crci.2014.08.005>
- 1459 Naseem S, Gevers B, Boldt R, et al (2019) Comparison of transition metal (Fe, Co, Ni, Cu, and Zn)  
1460 containing tri-metal layered double hydroxides (LDHs) prepared by urea hydrolysis. *RSC Adv*  
1461 9:3030–3040. <https://doi.org/10.1039/C8RA10165E>
- 1462 Ogawa M, Asai S (2000) Hydrothermal Synthesis of Layered Double Hydroxide–Deoxycholate  
1463 Intercalation Compounds. *Chem Mater* 12:3253–3255. <https://doi.org/10.1021/cm000455n>

- 1464 Othman MR, Rasid NM, Fernando WJN (2006) Effects of thermal treatment on the micro-structures  
1465 of co-precipitated and sol-gel synthesized (Mg-Al) hydrotalcites. *Microporous Mesoporous*  
1466 *Mater* 93:23–28. <https://doi.org/10.1016/j.micromeso.2006.02.007>
- 1467 Özacar M, Şengil İA (2002) Adsorption of Acid Dyes from Aqueous Solutions by Calcined Alunite and  
1468 Granular Activated Carbon. *Adsorption* 8:301–308.  
1469 <https://doi.org/10.1023/A:1021585413857>
- 1470 Palacio LA, Velásquez J, Echavarría A, et al (2010) Total oxidation of toluene over calcined trimetallic  
1471 hydrotalcites type catalysts. *J Hazard Mater* 177:407–413.  
1472 <https://doi.org/10.1016/j.jhazmat.2009.12.048>
- 1473 Palomares A, Lopez-Nieto JM, Lazaro FJ, et al (1999) Reactivity in the removal of SO<sub>2</sub> and NO<sub>x</sub> on  
1474 Co/Mg/Al mixed oxides derived from hydrotalcites. *Appl Catal B Environ* 20:257–266.  
1475 [https://doi.org/10.1016/S0926-3373\(98\)00121-0](https://doi.org/10.1016/S0926-3373(98)00121-0)
- 1476 Paredes SP, Fetter G, Bosch P, Bulbulian S (2006) Sol-gel synthesis of hydrotalcite — like compounds.  
1477 *J Mater Sci* 41:3377–3382. <https://doi.org/10.1007/s10853-005-5347-4>
- 1478 Park S, Kwon D, Kang JY, Jung JC (2018) Influence of the preparation method on the catalytic activity  
1479 of Mg Al hydrotalcites as solid base catalysts. *Green Energy Environ.*  
1480 <https://doi.org/10.1016/j.gee.2018.11.003>
- 1481 Pavan PC, Crepaldi EL, de A. Gomes G, Valim JB (1999) Adsorption of sodium dodecylsulfate on a  
1482 hydrotalcite-like compound. Effect of temperature, pH and ionic strength. *Colloids Surf*  
1483 *Physicochem Eng Asp* 154:399–410. [https://doi.org/10.1016/S0927-7757\(98\)00847-4](https://doi.org/10.1016/S0927-7757(98)00847-4)
- 1484 Pavan PC, Crepaldi EL, Valim JB (2000) Sorption of Anionic Surfactants on Layered Double Hydroxides.  
1485 *J Colloid Interface Sci* 229:346–352. <https://doi.org/10.1006/jcis.2000.7031>
- 1486 Perez-Lopez OW, Senger A, Marcilio NR, Lansarin MA (2006) Effect of composition and thermal  
1487 pretreatment on properties of Ni-Mg-Al catalysts for CO<sub>2</sub> reforming of methane. *Appl Catal*  
1488 *Gen* 303:234–244. <https://doi.org/10.1016/j.apcata.2006.02.024>
- 1489 Pinnavaia TJ, Amarasekera J, Polansky CA (1991) Process using sorbents for the removal of sox from  
1490 flue gas and other gas streams
- 1491 Pinnavaia TJ, Amarasekera J, Polansky CA (1992) Process using sorbents for the removal of SO<sub>x</sub> from  
1492 flue gas
- 1493 Prince J, Montoya A, Ferrat G, Valente JS (2009) Proposed General Sol-Gel Method to Prepare  
1494 Multimetallic Layered Double Hydroxides: Synthesis, Characterization, and Envisaged  
1495 Application. *Chem Mater* 21:5826–5835. <https://doi.org/10.1021/cm902741c>
- 1496 Prinetto F, Ghiotti G, Graffin P, Tichit D (2000) Synthesis and characterization of sol-gel Mg/Al and  
1497 Ni/Al layered double hydroxides and comparison with co-precipitated samples. *Microporous*  
1498 *Mesoporous Mater* 39:229–247. [https://doi.org/10.1016/S1387-1811\(00\)00197-9](https://doi.org/10.1016/S1387-1811(00)00197-9)
- 1499 Radha S, Navrotsky A (2014) Energetics of CO<sub>2</sub> Adsorption on Mg-Al Layered Double Hydroxides and  
1500 Related Mixed Metal Oxides. *J Phys Chem C* 118:29836–29844.  
1501 <https://doi.org/10.1021/jp508678k>

- 1502 Rahmanian O, Dinari M, Neamati S (2018) Synthesis and characterization of citrate intercalated  
1503 layered double hydroxide as a green adsorbent for Ni<sup>2+</sup> and Pb<sup>2+</sup> removal. *Environ Sci Pollut*  
1504 *Res* 25:36267–36277. <https://doi.org/10.1007/s11356-018-3584-8>
- 1505 Ram Reddy MK, Xu ZP, Diniz da Costa JC (2008) Influence of Water on High-Temperature CO<sub>2</sub>  
1506 Capture Using Layered Double Hydroxide Derivatives. *Ind Eng Chem Res* 47:2630–2635.  
1507 <https://doi.org/10.1021/ie0716060>
- 1508 Ram Reddy MK, Xu ZP, Lu GQ (Max), Diniz da Costa JC (2006) Layered Double Hydroxides for CO<sub>2</sub>  
1509 Capture: Structure Evolution and Regeneration. *Ind Eng Chem Res* 45:7504–7509.  
1510 <https://doi.org/10.1021/ie060757k>
- 1511 Ramírez-Moreno MJ, Romero-Ibarra IC, Hernández-Pérez MA, Pfeiffer H (2014) CO<sub>2</sub> Adsorption at  
1512 Elevated Pressure and Temperature on Mg–Al Layered Double Hydroxide. *Ind Eng Chem Res*  
1513 53:8087–8094. <https://doi.org/10.1021/ie5010515>
- 1514 Ramos E, Lopez T, Bosch P, et al (1997) Thermal stability of sol-gel hydrotalcites. *J Sol-Gel Sci Technol*  
1515 8:437–442. <https://doi.org/10.1007/BF02436879>
- 1516 Ramos-Ramírez E, Ortega NLG, Soto CAC, Gutiérrez MTO (2009) Adsorption isotherm studies of  
1517 chromium (VI) from aqueous solutions using sol–gel hydrotalcite-like compounds. *J Hazard*  
1518 *Mater* 172:1527–1531. <https://doi.org/10.1016/j.jhazmat.2009.08.023>
- 1519 Rao MM, Reddy BR, Jayalakshmi M, et al (2005) Hydrothermal synthesis of Mg–Al hydrotalcites by  
1520 urea hydrolysis. *Mater Res Bull* 40:347–359.  
1521 <https://doi.org/10.1016/j.materresbull.2004.10.007>
- 1522 Roelofs JCAA, Lensveld DJ, van Dillen AJ, de Jong KP (2001) On the Structure of Activated  
1523 Hydrotalcites as Solid Base Catalysts for Liquid-Phase Aldol Condensation. *J Catal* 203:184–  
1524 191. <https://doi.org/10.1006/jcat.2001.3295>
- 1525 Rosatella AA, Simeonov SP, Frade RFM, Afonso CAM (2011) 5-Hydroxymethylfurfural (HMF) as a  
1526 building block platform: Biological properties, synthesis and synthetic applications. *Green*  
1527 *Chem* 13:754. <https://doi.org/10.1039/c0gc00401d>
- 1528 Rubí H, Fall C, Ortega RE (2009) Pollutant removal from oily wastewater discharged from car washes  
1529 through sedimentation–coagulation. *Water Sci Technol* 59:2359–2369.  
1530 <https://doi.org/10.2166/wst.2009.307>
- 1531 Sakano M, Kawamura S (2018) Method for producing NO<sub>x</sub> storage-reduction catalyst
- 1532 Sato T, Fujita H, Endo T, Shimada M (1988) Synthesis Of Hydrotalcite-Like Compounds And Their  
1533 Physico-Chemical Properties. *React Solids* 5:219–228
- 1534 Sedlmair Ch, Seshan K, Jentys A, Lercher JA (2003) Elementary steps of NO<sub>x</sub> adsorption and surface  
1535 reaction on a commercial storage–reduction catalyst. *J Catal* 214:308–316.  
1536 [https://doi.org/10.1016/S0021-9517\(02\)00085-4](https://doi.org/10.1016/S0021-9517(02)00085-4)
- 1537 Seftel EM, Niarchos M, Mitropoulos Ch, et al (2015) Photocatalytic removal of phenol and  
1538 methylene-blue in aqueous media using TiO<sub>2</sub>@LDH clay nanocomposites. *Catal Today*  
1539 252:120–127. <https://doi.org/10.1016/j.cattod.2014.10.030>



- 1540 Seki Y, Yurdakoç K (2005) Paraquat adsorption onto clays and organoclays from aqueous solution. *J*  
1541 *Colloid Interface Sci* 287:1–5. <https://doi.org/10.1016/j.jcis.2004.10.072>
- 1542 Shan R, Yan L, Yang K, et al (2014) Magnetic Fe<sub>3</sub>O<sub>4</sub>/MgAl-LDH composite for effective removal of  
1543 three red dyes from aqueous solution. *Chem Eng J* 252:38–46.  
1544 <https://doi.org/10.1016/j.cej.2014.04.105>
- 1545 Sharma SK, Kushwaha PK, Srivastava VK, et al (2007) Effect of Hydrothermal Conditions on Structural  
1546 and Textural Properties of Synthetic Hydrotalcites of Varying Mg/Al Ratio. *Ind Eng Chem Res*  
1547 46:4856–4865. <https://doi.org/10.1021/ie061438w>
- 1548 Sheng T, Zhang Z, Hu Y, et al (2019) Adsorption of phosphorus by using magnetic Mg–Al-, Zn–Al- and  
1549 Mg–Fe-layered double hydroxides: comparison studies and adsorption mechanism. *Environ*  
1550 *Sci Pollut Res* 26:7102–7114. <https://doi.org/10.1007/s11356-019-04191-5>
- 1551 Sikander U, Samsudin MF, Sufian S, et al (2018) Tailored hydrotalcite-based Mg-Ni-Al catalyst for  
1552 hydrogen production via methane decomposition: Effect of nickel concentration and spinel-  
1553 like structures. *Int J Hydrog Energy*. <https://doi.org/10.1016/j.ijhydene.2018.10.224>
- 1554 Sikander U, Sufian S, Salam MA (2017) A review of hydrotalcite based catalysts for hydrogen  
1555 production systems. *Int J Hydrog Energy* 42:19851–19868.  
1556 <https://doi.org/10.1016/j.ijhydene.2017.06.089>
- 1557 Silletti BA, Adams RT, Sigmon SM, et al (2006) A novel Pd/MgAlO<sub>x</sub> catalyst for NO<sub>x</sub> storage-reduction.  
1558 *Catal Today* 114:64–71. <https://doi.org/10.1016/j.cattod.2006.02.003>
- 1559 Silva JM, Trujillano R, Rives V, et al (2017) High temperature CO<sub>2</sub> sorption over modified  
1560 hydrotalcites. *Chem Eng J* 325:25–34. <https://doi.org/10.1016/j.cej.2017.05.032>
- 1561 Smalenskaite A, Vieira DEL, Salak AN, et al (2017) A comparative study of co-precipitation and sol-gel  
1562 synthetic approaches to fabricate cerium-substituted Mg Al layered double hydroxides with  
1563 luminescence properties. *Appl Clay Sci* 143:175–183.  
1564 <https://doi.org/10.1016/j.clay.2017.03.036>
- 1565 Solovov VA, Nikolenko NV, Kovalenko VL, et al (2018) Synthesis of Ni(II)-Ti(IV) Layered Double  
1566 Hydroxides using Coprecipitation at High Supersaturation Method. *J Eng Appl Sci* 13:9652–  
1567 9656
- 1568 Song W, Wang X, Wang Q, et al (2015) Plasma-induced grafting of polyacrylamide on graphene oxide  
1569 nanosheets for simultaneous removal of radionuclides. *Phys Chem Chem Phys* 17:398–406.  
1570 <https://doi.org/10.1039/C4CP04289A>
- 1571 Sun Y, Wang X, Ai Y, et al (2017) Interaction of sulfonated graphene oxide with U(VI) studied by  
1572 spectroscopic analysis and theoretical calculations. *Chem Eng J* 310:292–299.  
1573 <https://doi.org/10.1016/j.cej.2016.10.122>
- 1574 Tanasoi S, Tanchoux N, Urdă A, et al (2009) New Cu-based mixed oxides obtained from LDH  
1575 precursors, catalysts for methane total oxidation. *Appl Catal Gen* 363:135–142.  
1576 <https://doi.org/10.1016/j.apcata.2009.05.007>
- 1577 Tang N, He T, Liu J, et al (2018) New Insights into CO<sub>2</sub> Adsorption on Layered Double Hydroxide  
1578 (LDH)-Based Nanomaterials. *Nanoscale Res Lett* 13:. [https://doi.org/10.1186/s11671-018-](https://doi.org/10.1186/s11671-018-2471-z)  
1579 2471-z

- 1580 Thevenot F, Szymanski R, Chaumette P (1989) PREPARATION AND CHARACTERIZATION OF Al-RICH  
1581 Zn-Al HYDROTALCITE-LIKE COMPOUNDS. *Clays Clay Miner* 37:7
- 1582 Thomas N (2012) Mechanochemical synthesis of layered hydroxy salts. *Mater Res Bull* 47:3568–3572.  
1583 <https://doi.org/10.1016/j.materresbull.2012.06.057>
- 1584 Thouchprasitchaia N, Pintuyothin N, Pongstabodee S (2018) Optimization of CO<sub>2</sub> adsorption capacity  
1585 and cyclical adsorption/desorption on tetraethylenepentamine-supported surface-modified  
1586 hydrotalcite. *J Environ Sci* 65:293–305. <https://doi.org/10.1016/j.jes.2017.02.015>
- 1587 Tichit D, Rolland A, Prinetto F, et al (2002) Comparison of the structural and acid–base properties of  
1588 Ga- and Al-containing layered double hydroxides obtained by microwave irradiation and  
1589 conventional ageing of synthesis gels. *J Mater Chem* 12:3832–3838.  
1590 <https://doi.org/10.1039/B203376N>
- 1591 Tsuji M, Mao G, Yoshida T, Tamaura Y (1993) Hydrotalcites with an extended Al<sup>3+</sup>-substitution:  
1592 Synthesis, simultaneous TG-DTA-MS study, and their CO<sub>2</sub> adsorption behaviors. *J Mater Res*  
1593 8:1137–1142. <https://doi.org/10.1557/JMR.1993.1137>
- 1594 Tzompantzi F, Mantilla A, Bañuelos F, et al (2011) Improved Photocatalytic Degradation of Phenolic  
1595 Compounds With ZnAl Mixed Oxides Obtained from LDH Materials. *Top Catal* 54:257–263.  
1596 <https://doi.org/10.1007/s11244-011-9656-3>
- 1597 Ulibarri M (2001) Adsorption of anionic species on hydrotalcite-like compounds: effect of interlayer  
1598 anion and crystallinity. *Appl Clay Sci* 18:17–27. [https://doi.org/10.1016/S0169-1317\(00\)00026-0](https://doi.org/10.1016/S0169-1317(00)00026-0)
- 1600 Umeno T, Hanzama M, Hayashi Y (2019) NO<sub>x</sub> storage reduction catalyst for purifying exhaust gas and  
1601 exhaust gas purification method using said catalyst
- 1602 Valeikiene L, Paitian R, Grigoraviciute-Puroniene I, et al (2019) Transition metal substitution effects in  
1603 sol-gel derived Mg<sub>3-x</sub>M<sub>x</sub>/Al<sub>1</sub> (M = Mn, Co, Ni, Cu, Zn) layered double hydroxides. *Mater*  
1604 *Chem Phys* 237:121863. <https://doi.org/10.1016/j.matchemphys.2019.121863>
- 1605 Valente JS, Cantú MS, Cortez JGH, et al (2007) Preparation and Characterization of Sol–Gel MgAl  
1606 Hydrotalcites with Nanocapsular Morphology. *J Phys Chem C* 111:642–651.  
1607 <https://doi.org/10.1021/jp065283h>
- 1608 Valente JS, Lima E, Toledo-Antonio JA, et al (2010) Comprehending the Thermal Decomposition and  
1609 Reconstruction Process of Sol–Gel MgAl Layered Double Hydroxides. *J Phys Chem C*  
1610 114:2089–2099. <https://doi.org/10.1021/jp910538r>
- 1611 Valente JS, Prince J, Maubert AM, et al (2009) Physicochemical Study of Nanocapsular Layered  
1612 Double Hydroxides Evolution. *J Phys Chem C* 113:5547–5555.  
1613 <https://doi.org/10.1021/jp810293y>
- 1614 Valente JS, Quintana-Solorzano R (2011) Novel SO<sub>x</sub> removal catalysts for the FCC process:  
1615 Manufacture method, characterization, and pilot-scale testing. *Energy Environ Sci* 4:4096.  
1616 <https://doi.org/10.1039/c1ee01197a>
- 1617 van Putten R-J, van der Waal JC, de Jong E, et al (2013) Hydroxymethylfurfural, A Versatile Platform  
1618 Chemical Made from Renewable Resources. *Chem Rev* 113:1499–1597.  
1619 <https://doi.org/10.1021/cr300182k>

- 1620 Vierheilig A (2003) Compounds, compositions and methods to reduce SO<sub>x</sub> emissions from FCC units
- 1621 Wan S, Wang S, Li Y, Gao B (2017) Functionalizing biochar with Mg–Al and Mg–Fe layered double  
1622 hydroxides for removal of phosphate from aqueous solutions. *J Ind Eng Chem* 47:246–253.  
1623 <https://doi.org/10.1016/j.jiec.2016.11.039>
- 1624 Wang J, Stevens LA, Drage TC, et al (2012a) Preparation and CO<sub>2</sub> adsorption of amine modified  
1625 layered double hydroxide via anionic surfactant-mediated route. *Chem Eng J* 181–182:267–  
1626 275. <https://doi.org/10.1016/j.ces.2011.11.078>
- 1627 Wang J, Stevens LA, Drage TC, Wood J (2012b) Preparation and CO<sub>2</sub> adsorption of amine modified  
1628 Mg–Al LDH via exfoliation route. *Chem Eng Sci* 68:424–431.  
1629 <https://doi.org/10.1016/j.ces.2011.09.052>
- 1630 Wang Q, Tay HH, Ng DJW, et al (2010) The Effect of Trivalent Cations on the Performance of Mg–M–  
1631 CO<sub>3</sub> Layered Double Hydroxides for High-Temperature CO<sub>2</sub> Capture. *ChemSusChem* 3:965–  
1632 973. <https://doi.org/10.1002/cssc.201000099>
- 1633 Wang R, Wu X, Zou C, et al (2018) NO<sub>x</sub> Removal by Selective Catalytic Reduction with Ammonia over  
1634 a Hydrotalcite-Derived NiFe Mixed Oxide. *Catalysts* 8:384.  
1635 <https://doi.org/10.3390/catal8090384>
- 1636 Wang X, Sun Y, Alsaedi A, et al (2015) Interaction mechanism of Eu(III) with MX-80 bentonite studied  
1637 by batch, TRLFS and kinetic desorption techniques. *Chem Eng J* 264:570–576.  
1638 <https://doi.org/10.1016/j.ces.2014.11.136>
- 1639 Wang Y, Du T, Liu L, et al (2017) A Review of Layered Double Hydroxides as Intermediate-  
1640 temperature CO<sub>2</sub> Adsorbents. In: *Proceedings of the 2017 6th International Conference on*  
1641 *Energy, Environment and Sustainable Development (ICEESD 2017)*. Atlantis Press, Zhuhai,  
1642 China
- 1643 Wang Z, Liu F, Lu C (2011) Mg–Al–carbonate layered double hydroxides as a novel catalyst of luminol  
1644 chemiluminescence. *Chem Commun* 47:5479. <https://doi.org/10.1039/c1cc10520e>
- 1645 Wu L, Peng B, Li Q, et al (2019a) Formation of high crystalline LDH sludge for removing Cu and Zn  
1646 from wastewater by controlled double-jet precipitation. *Environ Sci Pollut Res* 26:19665–  
1647 19675. <https://doi.org/10.1007/s11356-019-05161-7>
- 1648 Wu X, Wang R, Du Y, et al (2019b) NO<sub>x</sub> removal by selective catalytic reduction with ammonia over  
1649 hydrotalcite-derived NiTi mixed oxide. *New J Chem* 43:2640–2648.  
1650 <https://doi.org/10.1039/C8NJ05280H>
- 1651 Wu Y-J, Li P, Yu J-G, et al (2013) K-Promoted Hydrotalcites for CO<sub>2</sub> Capture in Sorption Enhanced  
1652 Reactions. *Chem Eng Technol* 36:567–574. <https://doi.org/10.1002/ceat.201200694>
- 1653 Xu S, Liao M, Zeng H, et al (2016) Preparation Behavior of the Mg–Fe Hydrotalcite by Urea Method  
1654 and Its Cr(VI) Sorption Property. *J Nanosci Nanotechnol* 16:3122–3131.  
1655 <https://doi.org/10.1166/jnn.2016.12411>
- 1656 Xu ZP, Lu GQ (Max) (2005) Hydrothermal Synthesis of Layered Double Hydroxides (LDHs) from Mixed  
1657 MgO and Al<sub>2</sub>O<sub>3</sub>: LDH Formation Mechanism. *Chem Mater* 17:1055–1062.  
1658 <https://doi.org/10.1021/cm048085g>

- 1659 Xu ZP, Zhang J, Adebajo MO, et al (2011) Catalytic applications of layered double hydroxides and  
1660 derivatives. *Appl Clay Sci* 53:139–150. <https://doi.org/10.1016/j.clay.2011.02.007>
- 1661 Xue L, Gao B, Wan Y, et al (2016) High efficiency and selectivity of MgFe-LDH modified wheat-straw  
1662 biochar in the removal of nitrate from aqueous solutions. *J Taiwan Inst Chem Eng* 63:312–  
1663 317. <https://doi.org/10.1016/j.jtice.2016.03.021>
- 1664 Yang D, Song S, Zou Y, et al (2017) Rational design and synthesis of monodispersed hierarchical SiO<sub>2</sub>  
1665 @layered double hydroxide nanocomposites for efficient removal of pollutants from  
1666 aqueous solution. *Chem Eng J* 323:143–152. <https://doi.org/10.1016/j.cej.2017.03.158>
- 1667 Yang L, Shahrivari Z, Liu PKT, et al (2005) Removal of Trace Levels of Arsenic and Selenium from  
1668 Aqueous Solutions by Calcined and Uncalcined Layered Double Hydroxides (LDH). *Ind Eng*  
1669 *Chem Res* 44:6804–6815. <https://doi.org/10.1021/ie049060u>
- 1670 Yang P, Yu J, Wang Z, et al (2004) Urea method for the synthesis of hydrotalcites. *React Kinet Catal*  
1671 *Lett* 83:275–282. <https://doi.org/10.1023/B:REAC.0000046087.86802.c2>
- 1672 Yang R, Gao Y, Wang J, Wang Q (2014) Layered double hydroxide (LDH) derived catalysts for  
1673 simultaneous catalytic removal of soot and NO<sub>x</sub>. *Dalton Trans* 43:10317.  
1674 <https://doi.org/10.1039/c3dt52896k>
- 1675 Yang S, Ren X, Zhao G, et al (2015) Competitive sorption and selective sequence of Cu(II) and Ni(II) on  
1676 montmorillonite: Batch, modeling, EPR and XAS studies. *Geochim Cosmochim Acta* 166:129–  
1677 145. <https://doi.org/10.1016/j.gca.2015.06.020>
- 1678 Yang Z, Choi K-M, Jiang N, Park S-E (2007) Microwave Synthesis of Hydrotalcite by Urea Hydrolysis.  
1679 *Bull Korean Chem Soc* 28:2029–2033
- 1680 Yang Z, Wei J, Zeng G, et al (2019) A review on strategies to LDH-based materials to improve  
1681 adsorption capacity and photoreduction efficiency for CO<sub>2</sub>. *Coord Chem Rev* 386:154–182.  
1682 <https://doi.org/10.1016/j.ccr.2019.01.018>
- 1683 Yokomichi Y, Nakayama T, Okada O, et al (1996) Fundamental study on the NO<sub>x</sub> direct decomposition  
1684 catalysts. *Catal Today* 29:155–160. [https://doi.org/10.1016/0920-5861\(95\)00252-9](https://doi.org/10.1016/0920-5861(95)00252-9)
- 1685 Yong Z, Mata V, Rodrigues A (2002) Adsorption of carbon dioxide at high temperature—a review. *Sep*  
1686 *Purif Technol* 26:195–205. [https://doi.org/10.1016/S1383-5866\(01\)00165-4](https://doi.org/10.1016/S1383-5866(01)00165-4)
- 1687 Yoo JS, Bhattacharyya AA, Radlowski CA, Karch JA (1992) Advanced De-SO<sub>x</sub> catalyst: Mixed solid  
1688 solution spinels with cerium oxide. *Appl Catal B Environ* 1:169–189.  
1689 [https://doi.org/10.1016/0926-3373\(92\)80022-R](https://doi.org/10.1016/0926-3373(92)80022-R)
- 1690 Yu J, Cheng J, Ma C, et al (2009) NO<sub>x</sub> decomposition, storage and reduction over novel mixed oxide  
1691 catalysts derived from hydrotalcite-like compounds. *J Colloid Interface Sci* 333:423–30.  
1692 <https://doi.org/10.1016/j.jcis.2009.02.022>
- 1693 Yu JJ, Jiang Z, Zhu L, et al (2006) Adsorption/Desorption Studies of NO<sub>x</sub> on Well-Mixed Oxides  
1694 Derived from Co–Mg/Al Hydrotalcite-like Compounds. *J Phys Chem B* 110:4291–4300.  
1695 <https://doi.org/10.1021/jp056473f>

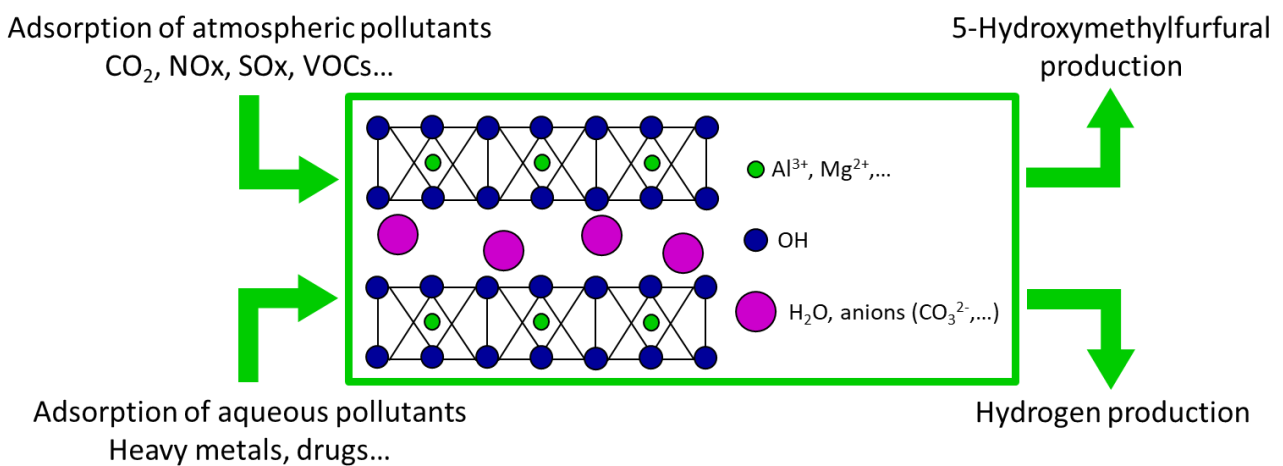
- 1696 Yu JJ, Wang XP, Tao YX, et al (2007) Effective NO<sub>x</sub> Decomposition and Storage/Reduction over  
 1697 Mixed Oxides Derived from Layered Double Hydroxides. *Ind Eng Chem Res* 46:5794–5797.  
 1698 <https://doi.org/10.1021/ie0705958>
- 1699 Yu S, Wang X, Chen Z, et al (2017) Layered double hydroxide intercalated with aromatic acid anions  
 1700 for the efficient capture of aniline from aqueous solution. *J Hazard Mater* 321:111–120.  
 1701 <https://doi.org/10.1016/j.jhazmat.2016.09.009>
- 1702 Yu Y, Li X, Krishna R, et al (2018) Enhancing CO<sub>2</sub> Adsorption and Separation Properties of  
 1703 Aluminophosphate Zeolites by Isomorphous Heteroatom Substitutions. *ACS Appl Mater*  
 1704 *Interfaces* 10:43570–43577. <https://doi.org/10.1021/acsami.8b11235>
- 1705 Zakrzewska ME, Bogel-Łukasik E, Bogel-Łukasik R (2011) Ionic Liquid-Mediated Formation of 5-  
 1706 Hydroxymethylfurfural—A Promising Biomass-Derived Building Block. *Chem Rev* 111:397–  
 1707 417. <https://doi.org/10.1021/cr100171a>
- 1708 Zardin L, Perez-Lopez OW (2017) Hydrogen production by methane decomposition over Co-Al mixed  
 1709 oxides derived from hydrotalcites: Effect of the catalyst activation with H<sub>2</sub> or CH<sub>4</sub>. *Int J*  
 1710 *Hydrog Energy* 42:7895–7907. <https://doi.org/10.1016/j.ijhydene.2017.02.153>
- 1711 Zeng H-Y, Deng X, Wang Y-J, Liao K-B (2009a) Preparation of Mg-Al hydrotalcite by urea method and  
 1712 its catalytic activity for transesterification. *AIChE J* 55:1229–1235.  
 1713 <https://doi.org/10.1002/aic.11722>
- 1714 Zeng W, Cheng D, Chen F, Zhan X (2009b) Catalytic Conversion of Glucose on Al–Zr Mixed Oxides in  
 1715 Hot Compressed Water. *Catal Lett* 133:221–226. <https://doi.org/10.1007/s10562-009-0160-3>
- 1716 Zepp RG, Schlotzhauer PF (1981) Effects of equilibration time on photoreactivity of the pollutant DDE  
 1717 sorbed on natural sediments. *Chemosphere* 10:453–460. [https://doi.org/10.1016/0045-6535\(81\)90145-4](https://doi.org/10.1016/0045-6535(81)90145-4)
- 1719 Zhang WH, Guo XD, He J, Qian ZY (2008) Preparation of Ni(II)/Ti(IV) layered double hydroxide at high  
 1720 supersaturation. *J Eur Ceram Soc* 28:1623–1629.  
 1721 <https://doi.org/10.1016/j.jeurceramsoc.2007.11.016>
- 1722 Zhang Z-Q, Liao M-C, Zeng H-Y, et al (2014) Mg–Al hydrotalcites as solid base catalysts for alcoholysis  
 1723 of propylene oxide. *Fuel Process Technol* 128:519–524.  
 1724 <https://doi.org/10.1016/j.fuproc.2014.08.015>
- 1725 Zhao P, Liu X, Tian W, et al (2015) Adsorbilization of 2,4,6-trichlorophenol from aqueous solution by  
 1726 surfactant intercalated ZnAl layered double hydroxides. *Chem Eng J* 279:597–604.  
 1727 <https://doi.org/10.1016/j.cej.2015.05.037>
- 1728 Zhao R, Yin C, Zhao H, Liu C (2003) Synthesis, characterization, and application of hydrotalcites in  
 1729 hydrodesulfurization of FCC gasoline. *Fuel Process Technol* 81:201–209.  
 1730 [https://doi.org/10.1016/S0378-3820\(03\)00012-2](https://doi.org/10.1016/S0378-3820(03)00012-2)
- 1731 Zou Y, Wang X, Ai Y, et al (2016a) Coagulation Behavior of Graphene Oxide on Nanocrystalline  
 1732 Mg/Al Layered Double Hydroxides: Batch Experimental and Theoretical Calculation Study.  
 1733 *Environ Sci Technol* 50:3658–3667. <https://doi.org/10.1021/acs.est.6b00255>

1734 Zou Y, Wang X, Chen Z, et al (2016b) Superior coagulation of graphene oxides on nanoscale layered  
1735 double hydroxides and layered double oxides. Environ Pollut 219:107–117.  
1736 <https://doi.org/10.1016/j.envpol.2016.10.052>

1737 Zou Y, Wang X, Wu F, et al (2017) Controllable Synthesis of Ca-Mg-Al Layered Double Hydroxides and  
1738 Calcined Layered Double Oxides for the Efficient Removal of U(VI) from Wastewater  
1739 Solutions. ACS Sustain Chem Eng 5:1173–1185.  
1740 <https://doi.org/10.1021/acssuschemeng.6b02550>

1741

1742 **List of figures**

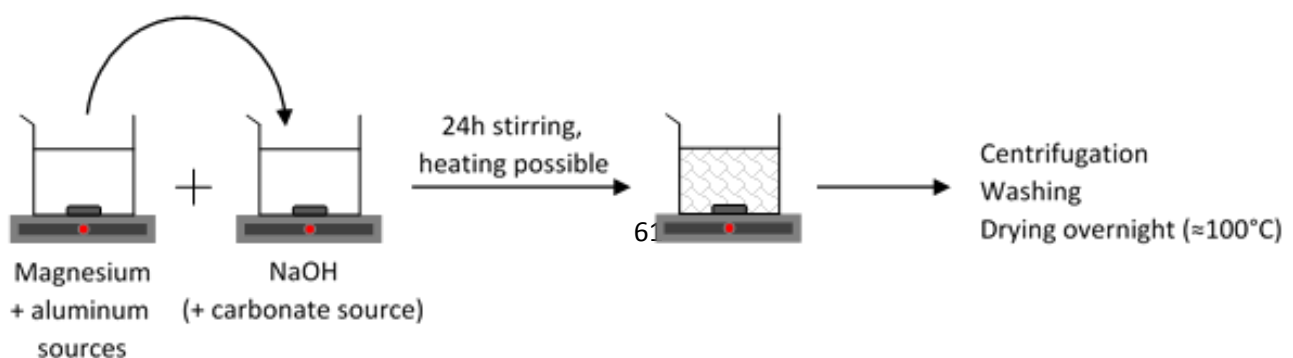


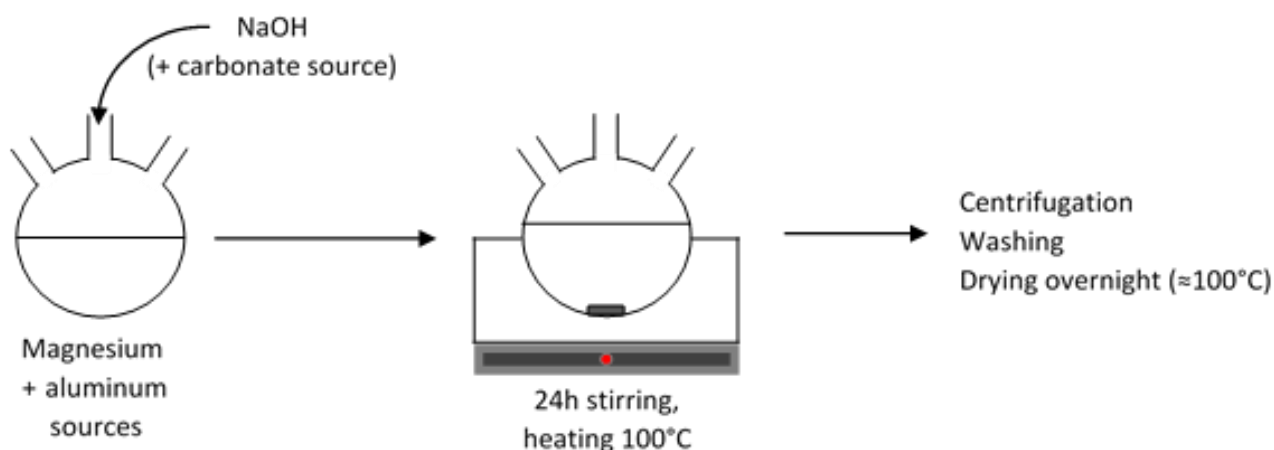
1743

1744 **Fig1.** Environmental applications of hydrotalcites discussed in this review.

1745

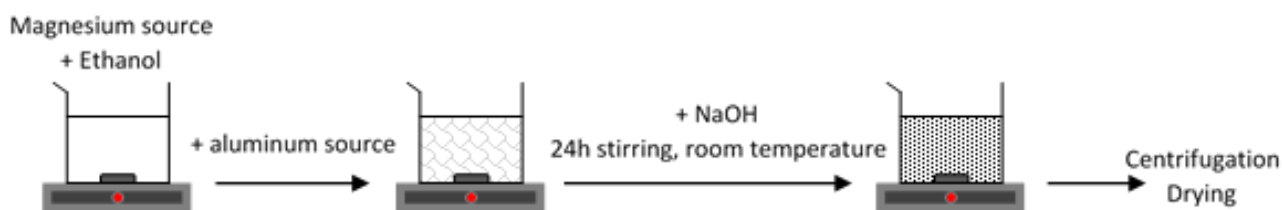
1746 **Fig2.** Scheme of the **co-precipitation** method applied to the LDHs synthesis.





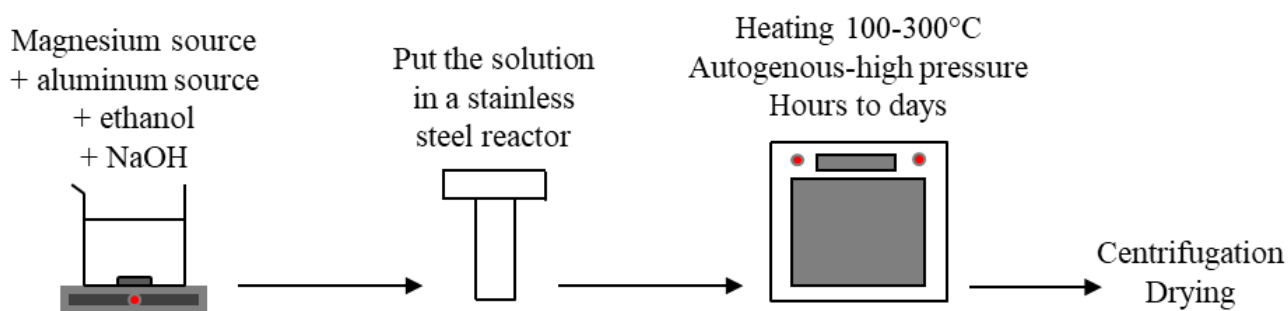
1747

1748 **Fig3.** Scheme of the synthesis of hydroxalclites via urea hydrolysis.



1749

1750 **Fig4.** Scheme of the synthesis of hydroxalclites by sol-gel process.



1751

1752 **Fig5.** Hydrothermal synthesis process applied to hydroxalclite synthesis.

1753

1754 **Table 1.** Main structural and textural impacts of different synthesis processes on LDHs.

Synthesis method	Advantages	Drawbacks
<b>Co-precipitation</b>	<ul style="list-style-type: none"> <li>- High crystallinity with post-treatment</li> <li>- Easy insertion of metallic elements</li> </ul>	<ul style="list-style-type: none"> <li>- Large Particles (formation of aggregates)</li> <li>- Low specific surface area</li> </ul>
<b>Use of urea</b>	<ul style="list-style-type: none"> <li>- Large thin platelets</li> <li>- Narrow particle size distribution</li> </ul>	<ul style="list-style-type: none"> <li>- Formation of CO<sub>2</sub> by urea decomposition, formation of carbonates as counter-anions</li> </ul>
<b>Sol-gel</b>	<ul style="list-style-type: none"> <li>- High homogeneity</li> <li>- High purity</li> <li>- Small particles (nanoscale) = high specific surface area</li> <li>- Short times (hours)</li> </ul>	<ul style="list-style-type: none"> <li>- Low crystallinity</li> <li>- Additional treatments required (microwave irradiation, ultrasonication, or hydrothermal treatment)</li> </ul>
<b>Hydrothermal</b>	<ul style="list-style-type: none"> <li>- Increases crystallinity</li> <li>- Increases particle size</li> <li>- Increases purity</li> </ul>	<ul style="list-style-type: none"> <li>- High energy (heating) and time (hours to days) demand</li> <li>- More efficient as an additional treatment of other synthesis methods</li> </ul>

1755

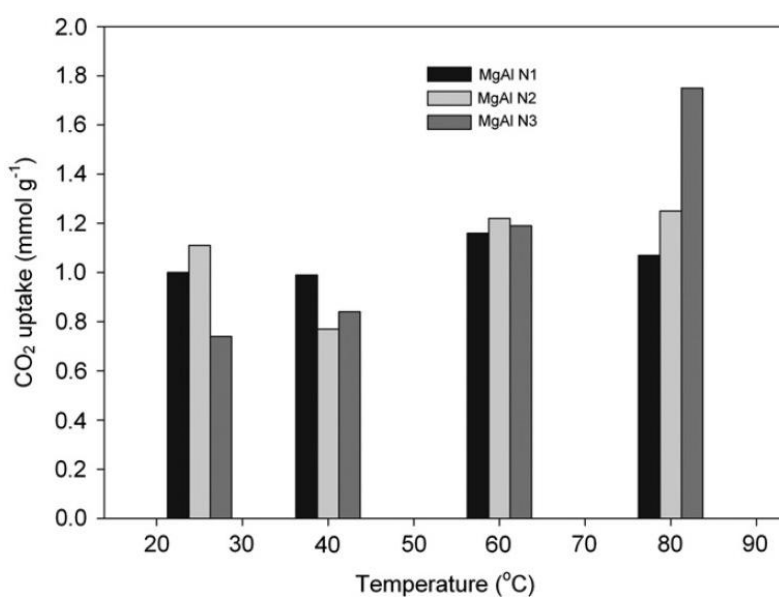
1756 **Table 2.** Synthesis parameters of the LDHs and mixed oxides cited in the part “2.1.1. CO<sub>2</sub>  
 1757 adsorption – Capture and storage”.

Reference	Type of material	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Adsorption capacity (mmol.g <sup>-1</sup> )	Synthesis method / structural modifications
<b>Mao and Tamaura 1993</b>	MgAlFe LDH	–	–	Co-precipitation at various Al/(Mg+Al) molar ratios.
<b>Tsuji et al. 1993</b>	Various LDHs	–	–	Co-precipitation with change of the M(II) cations: Mg <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Co <sup>2+</sup> .



<b>Wang et al. 2010</b>	Mg-M(III) LDHs	82.4 – 148.6	0.050 – 0.462	Co-precipitation with change of the M(III) cations: Al <sup>3+</sup> , Ga <sup>3+</sup> , Fe <sup>3+</sup> , Mn <sup>3+</sup> , Cr <sup>3+</sup> , Ce <sup>3+</sup> , La <sup>3+</sup> .
<b>Ram Reddy et al. 2006</b>	Calcined MgAl LDHs	63 – 167	0.231 – 0.486	Co-precipitation and calcination at different temperatures from 200 to 600°C for 4h.
<b>Ram Reddy et al. 2008</b>	Calcined MgAl LDHs	–	–	Co-precipitation and calcination at 400°C for 4h.
<b>Dadwhal et al. 2008</b>	Calcined MgAl LDHs	–	0.7	Co-precipitation and calcination at 500°C for 4h.
<b>León et al. 2010</b>	Calcined MgAl LDHs	62 – 190	0.4 – 1.15	Co-precipitation at low and high supersaturation and calcination at 450 or 700°C for 7h. Anion exchange by K <sup>+</sup> or Na <sup>+</sup> prior the calcination.
<b>Gao et al. 2013</b>	Calcined MgAl LDHs	154 – 239	0.30 – 0.72	Co-precipitation followed by hydrothermal treatment at 120°C for 6h, urea method, or urea decomposition followed by microwave irradiation at 120°C 200W for 30min.
<b>Ramírez-Moreno et al. 2014</b>	MgAl LDHs	136.6 – 296.3	0.2 – 0.75	Co-precipitation at low supersaturation.
<b>Bhatta et al. 2015</b>	MgAl LDH supported in coal-derived graphitic material	41 – 219.6	0.48 – 1.10	Co-precipitation at low supersaturation.

<b>Dantas et al. 2015</b>	MgAl LDHs expanded with a polymer	50.1 – 61.1	0.72 – 1.36	Co-precipitation at low supersaturation.
<b>Tang et al. 2018</b>	MgAl LDHs enlarged by SDS ions before grafting 3-APS	–	1.55 – 2.09	Co-precipitation at high supersaturation.
<b>Thouchprasitchaia et al. 2018</b>	TEPA-functionalized calcined MgAl LDHs (hydrotalcite)	5.7 – 165.2	2.03 – 6.03	Co-precipitation at low supersaturation.
<b>Wang et al. 2012b, a</b>	Amine-modified MgAl LDHs via exfoliation or anionic surfactant-mediated routes	–	0.75 – 1.8	Co-precipitation at high supersaturation.
<b>Wu et al. 2013</b>	K-promoted hydrotalcite	–	1.15	Commercial hydrotalcite.



1758

1759 **Fig6.** CO<sub>2</sub> adsorption by amine-modified MgAl hydrotalcites at different temperatures (from  
 1760 Wang et al. (2012b)).

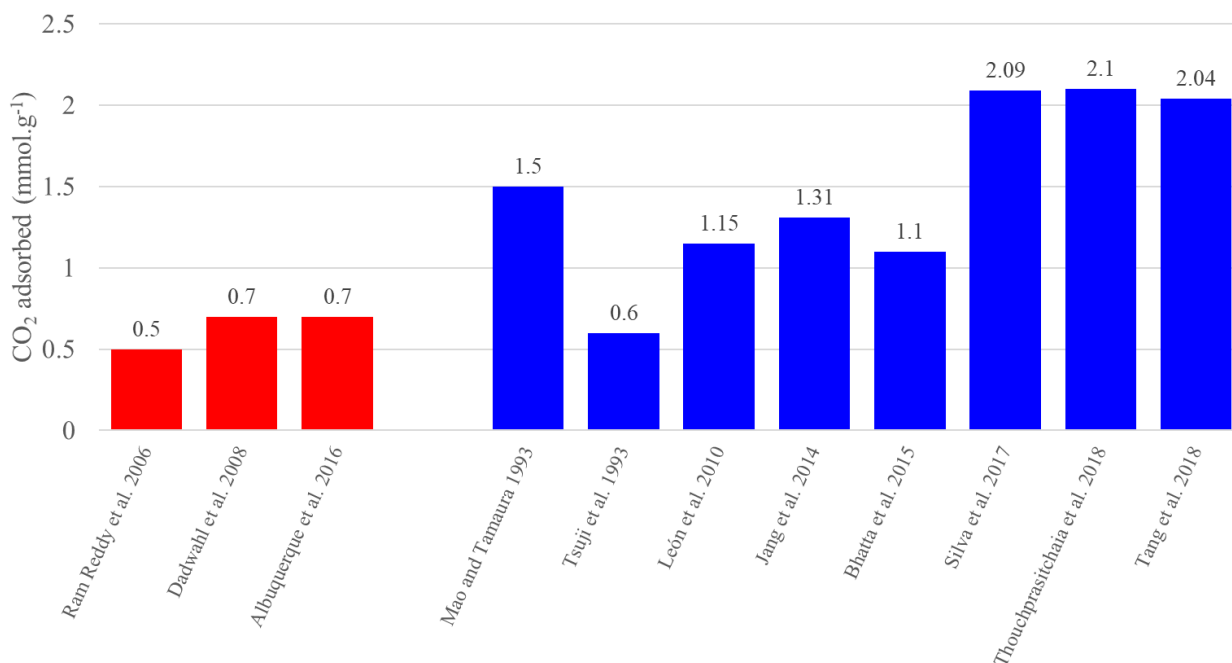
1761

1762 **Table 3.** CO<sub>2</sub> adsorption by several types of hydrotalcites according to literature.

M(II)/M(III) molar ratio	CO <sub>2</sub> adsorbed (mmol.g <sup>-1</sup> )	Synthesis process	Modifications / improvements	References
3	0.5	Co- precipitation	-	Ram Reddy et al. 2006
2.87	0.7	Co- precipitation	-	Dadwhal et al. 2008
2 – 3	0.7 – 1.5	Co- precipitation	-	Albuquerque et al. 2016
1 – 5	0.4 – 1.5	Co- precipitation	Fe-promoted	Mao and Tamaura 1993
1.2	0.15 – 0.6	Co- precipitation	Different M(II) cations	Tsuji et al. 1993
3	0.6 – 1.15	Co- precipitation	K- or Na-promoted	León et al. 2010

3	1.31	Hydrothermal	K-promoted	<b>Jang et al. 2014</b>
2	0.42 – 1.10	Co-precipitation	K-promoted	<b>Bhatta et al. 2015</b>
2	2.09	Co-precipitation	K-promoted + Ga substitution	<b>Silva et al. 2017</b>
3	2.1	Co-precipitation	TEPA-supported	<b>Thouchprasitthaia et al. 2018</b>
2 – 3	2.04	Co-precipitation	(3-AP)triethoxysilane-grafted	<b>Tang et al. 2018</b>

1763



1764

1765 **Fig7.** Comparison between non-modified (red) and modified (blue) hydrotalcites and derived  
 1766 materials on the CO<sub>2</sub> sorption capacity, according to Table 3.

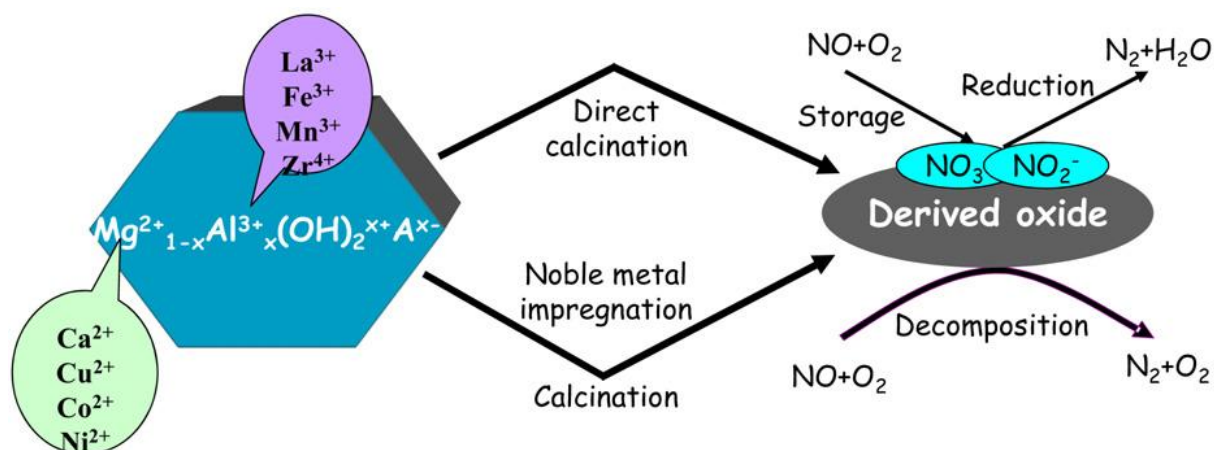
1767

1768 **Table 4.** Synthesis conditions of the LDHs and mixed oxides cited in the part “2.1.2. NO<sub>x</sub>  
 1769 and SO<sub>x</sub> adsorption”.

Reference	Type of	Surface area	Adsorption capacity	Synthesis method /
-----------	---------	--------------	---------------------	--------------------

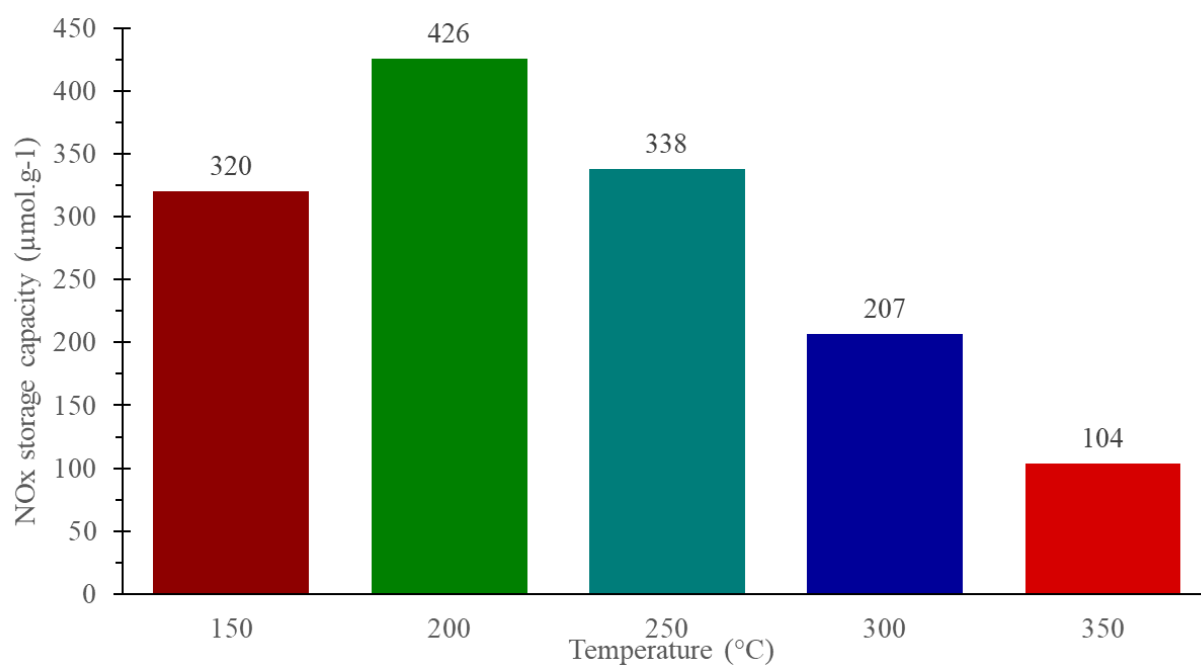
	<b>material</b>	<b>(m<sup>2</sup>.g<sup>-1</sup>)</b>	<b>(mmol.g<sup>-1</sup>)</b>	<b>structural modifications</b>
<b>Corma et al. 1994</b>	Calcined CuMgAl LDHs	–	–	<b>Co-precipitation</b> with fixed Mg/Al molar ratio at 3 and 10 molar% Cu, then calcination at 750°C for 3h.
<b>Palomares et al. 1999</b>	Calcined CuMgAl and CoMgAl LDHs	117 – 210	–	<b>Co-precipitation</b> similar to Corma et al. 1994b.
<b>Yu et al. 2006</b>	Calcined CoMgAl LDHs	21.6 – 162.7	–	<b>Co-precipitation</b> at low supersaturation with change of the Co/Mg molar ratio, then calcination at 800°C for 4h.
<b>Yu et al. 2007</b>	Calcined CaCoAl and CaCiLaAl LDHs	–	0.602 – 0.651	<b>Co-precipitation</b> at low supersaturation, then calcination at 800°C for 4h.
<b>Cheng et al. 2004</b>	Calcined MgAl LDHs impregnated with Pt	121 – 249	0.061 – 0.505	<b>Co-precipitation</b> at low supersaturation, then calcination at 600°C for 5h and impregnation with Pt(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> .
<b>Silletti et al. 2006</b>	Pd adsorbed on calcined commercial MgAl LDH	~ 190	0.003 – 0.062	Commercial LDH with a Mg:Al molar ratio of 7:3 calcined at 600°C, then [Pd(acac) <sub>2</sub> ] adsorbed on freshly calcined samples.
<b>Li et al. 2007</b>	Calcined MgRuAl LDHs	280	0.220	<b>Co-precipitation</b> at low supersaturation, then calcination at 600°C for 6h.
<b>Cui et al. 2019</b>	Calcined MnMgAl LDHs	108 – 144	0.104 – 0.426	<b>Co-precipitation</b> at low precipitation assisted by CTAB, then calcination at 600°C for 6h.

<b>Kameda et al. 2019a, b</b>	MgAl LDHs	–	–	Co-precipitation at low supersaturation.
<b>Cantú et al. 2005</b>	Calcined MgAl and MgFe LDHs	74 – 204	–	Co-precipitation at low supersaturation.



1770

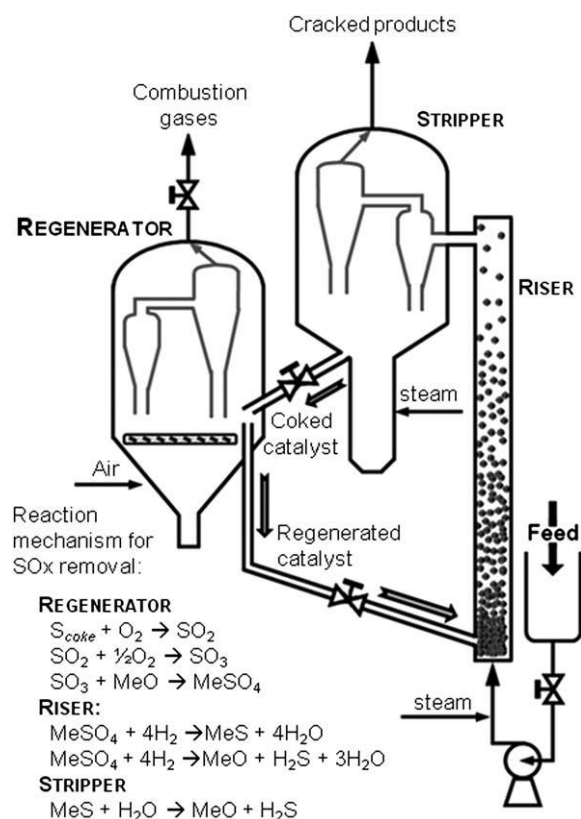
1771 **Fig8.** Schematic representation of LDH-derived catalysts for NO<sub>x</sub> storage and reduction  
 1772 (from Yu et al. 2009).



1773

1774 **Fig9.** NOx storage capacity at different temperatures of mixed oxides derived from MnMgAl

1775 LDHs containing 15 wt% Mn (from Cui et al. 2019).



1776

1777 **Fig10.** Simplified scheme of the Fluid Catalytic Cracking (FCC) process adapted to SO<sub>x</sub>  
 1778 removal (from Valente and Quintana-Solorzano 2011).

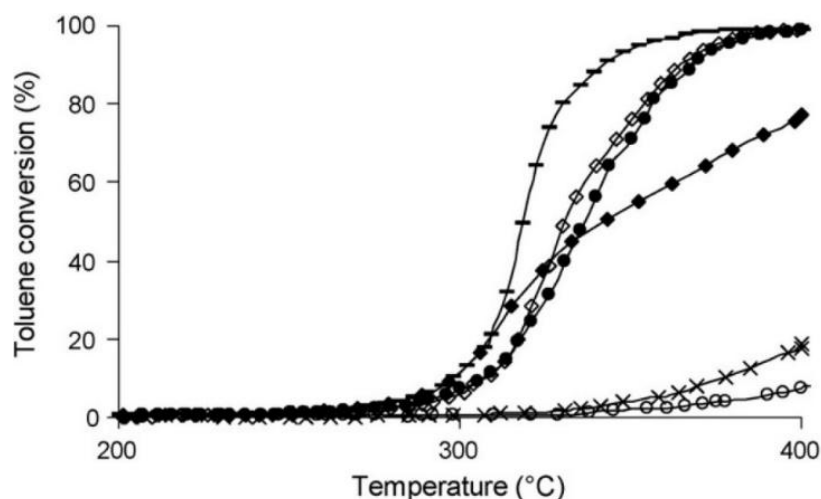
1779 **Table 5.** Synthesis parameters of the LDHs and mixed oxides cited in the part “2.1.3. VOCs  
 1780 total decomposition”.

Reference	Type of material	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Synthesis method
<b>Bahranowski et al. 1999</b>	Calcined CuCr, ZnCr, and CuAl LDHs	CuCr-LDHs : 10 – 20 ZnCr LDH : 41 CuAl LDH : 56	Co-precipitation at low supersaturation and calcination at 600°C for 3h. The CuCr-LDHs have been synthesized with M(II):M(III) molar ratios of 1:1, 2:1, and 3:1. ZnCr and CuAl were used to investigate separately the role of Cu and Cr.
<b>Mikulová et al. 2007</b>	Calcined NiAl LDH	52 – 161	Co-precipitation at low supersaturation and calcination at 450°C for 4h.



<b>Gennequin et al. 2009, 2010b</b>	Calcined CoMgAl LDHs	72 – 141	<b>Co-precipitation</b> at high supersaturation with varying Co:Mg:Al molar ratio of 6:0:2, 4:2:2, 2:4:2 and 0:6:2, and calcination at 500°C for 4h.
<b>Gennequin et al. 2010a</b>	Co-deposited calcined MgAl LDHs	3 – 233	<b>Co-precipitation</b> at high supersaturation, and calcination at different temperatures: 500, 600, 700, 800, and 900°C. Co was then deposited by aqueous impregnation method.
<b>Palacio et al. 2010</b>	Calcined MnCuAl and ZnCuAl LDHs	45 – 108	<b>Co-precipitation</b> at high supersaturation and calcination at 450 and 600°C.
<b>Dula et al. 2007</b>	Calcined MgMnAl LDHs	137 – 191	<b>Co-precipitation</b> at low supersaturation and calcination at 600°C for 4h. 2 different samples have been prepared with Mn either within the structure or in the ionic form as permanganate anions in the interlayer space.
<b>Tanasoi et al. 2009</b>	Calcined CuMgAl LDHs	114 – 188	<b>Co-precipitation</b> at low supersaturation with various copper content from 1 to 20 at%, and calcination at 750°C for 8h.
<b>Aguilera et al. 2011</b>	Calcined MnMgAl, CuMnMgAl and CoMnMgAl LDHs	75 – 249	<b>Co-precipitation</b> at low supersaturation with varying Cu/Mn and Co/Mn molar ratios of 0.5, 0.25, 0.1, and 0.05, and calcination at 500°C for 16h.
<b>Chmielarz et al. 2012</b>	Calcined CuMgAl, CoMgAl and CuCoMgAl LDHs	60 – 217	<b>Co-precipitation</b> at low supersaturation and calcination at 700 or 800°C. The samples calcined at 800°C were modified with potassium using aqueous impregnation method and calcined again at 600°C.
<b>Carpentier et al. 2002</b>	Calcined MgAl LDH with interlayer Pd complex	33 – 69	<b>Co-precipitation</b> at low supersaturation in presence of H <sub>2</sub> PdCl <sub>4</sub> and calcination at 290 and 500°C for 4h.
<b>Kovanda and JirátoVá</b>	Several calcined LDHs	28 – 150 (203 with Ni)	<b>Co-precipitation</b> at low supersaturation and calcination at 500°C for 4h. NiAl,

2011a, b			NiMn, CoAl, CoMn, NiCoAl, NiCoMn, NiCuAl, NiCuMn, CoCuAl, and CoCuMn have been obtained in order to compare with similar mixed oxides deposited on Al <sub>2</sub> O <sub>3</sub> /Al support.
----------	--	--	--

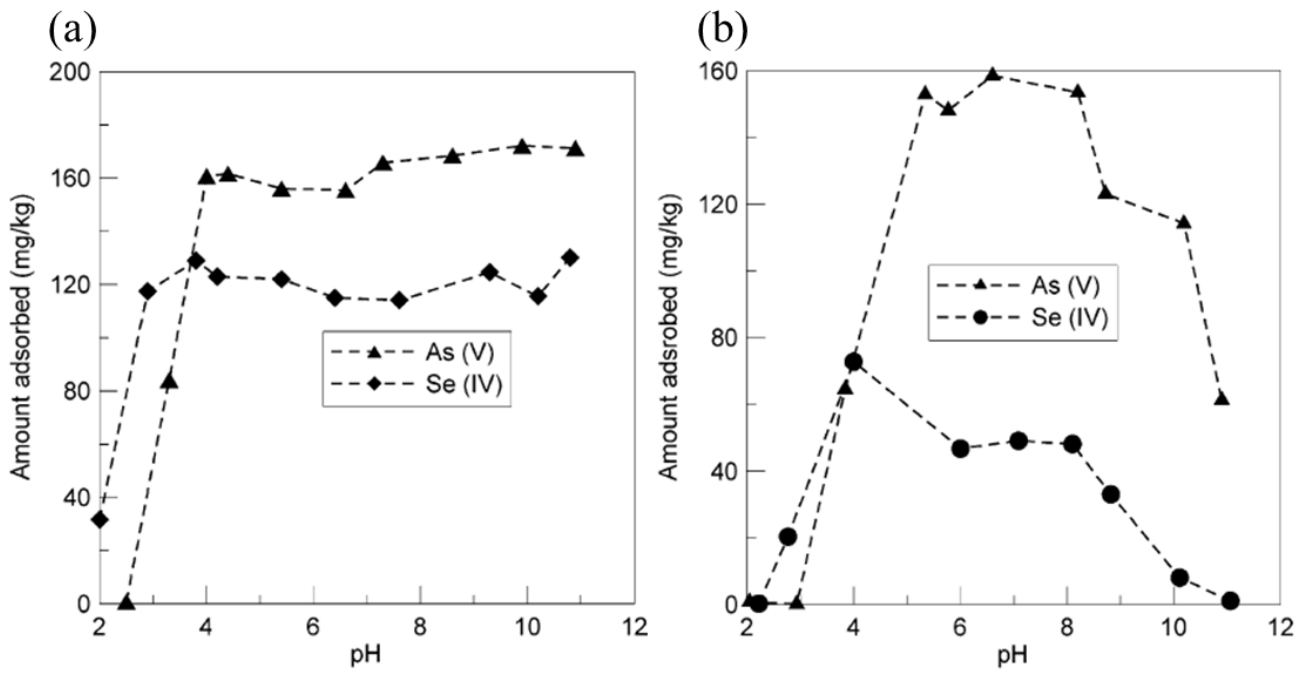


1781  
 1782 **Fig11.** Toluene conversion versus temperature for Co-containing hydrotalcites previously  
 1783 calcined at various temperatures (from Gennequin et al. (2010a)).

1784  
 1785 **Table 6.** Synthesis conditions of the LDHs and mixed oxides cited in the part “2.2.  
 1786 Adsorption of aqueous pollutants”.

Reference	Type of material	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Synthesis method
<b>Lehmann et al. 1999</b>	Commercial MgAl LDH (hydrotalcite)	34.8	Commercial hydrotalcite.
<b>Yang et al. 2005</b>	Calcined MgAl LDHs	47 – 198	Co-precipitation at high supersaturation, then calcination at 500°C for 4h.
<b>Lv et al. 2006</b>	Calcined MgAl, ZnAl, and NiAl LDHs	39.9 – 240.6	Synthesis method similar to co-precipitation with the use of urea, then calcination at various

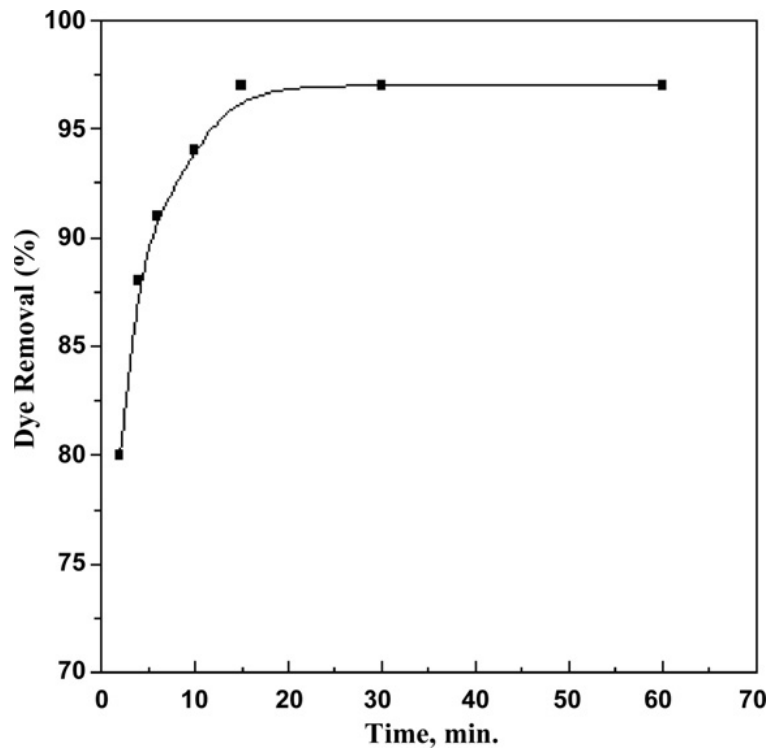
			temperatures (from 200 to 800°C).
<b>El-Sayed et al. 2016</b>	Calcined MgAlZn LDHs	65.1	Co-precipitation with 15 wt% Zn, then calcination at 450°C for 5h.
<b>Xue et al. 2016</b>	Biochar/MgFe LDHs	3.9 (pores filled by biochar)	LDH directly synthesized in presence of the biochar by the liquid-phase deposition method.
<b>Mahmoud et al. 2017</b>	Ti-Fe chitosan LDHs	146.5	Ball milling method for 10h at 300 rpm with titanium isopropoxide, iron nitrate, and chitosan.
<b>Yang et al. 2017</b>	SiO <sub>2</sub> supported on MgAl LDHs	–	In situ co-precipitation method at high supersaturation.
<b>Zou et al. 2017</b>	Calcined CaMgAl LDHs	43 – 157.8	Hydrothermal synthesis, then calcination at various temperatures (from 200 to 600°C) for 3h.
<b>Tzompantzi et al. 2011</b>	Calcined ZnAl LDHs	155 – 228	Co-precipitation at low supersaturation with different Zn/Al molar ratios, then calcination at 400°C for 12h.
<b>Seftel et al. 2015</b>	Various LDHs containing Zn <sup>2+</sup> , Cu <sup>2+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup> or Ti <sup>4+</sup>	5 – 230	Co-precipitation at low supersaturation with various M(II)/M(III) molar ratios.
<b>Ahmed and Gasser 2012</b>	MgFe LDHs with Cl <sup>-</sup> or CO <sub>3</sub> <sup>2-</sup> as compensating anion	–	Separate nucleation and aging method with colloid mill rotating at 5000 rpm for 3min.
<b>de Sá et al. 2013</b>	CaAl LDHs	–	Co-precipitation at high supersaturation.
<b>Shan et al. 2014</b>	Magnetic Fe <sub>3</sub> O <sub>4</sub> /MgAl LDHs	133	Co-precipitation at low supersaturation.
<b>Li et al. 2016</b>	MgAl LDHs	uncalcined : 24.7 calcined : 165.1	Low temperature ethanol-water mediated solvothermal method in an autoclave at 190°C for 1h.



1787

1788 **Fig12.** Effect of pH on the uptake of As(V) and Se(IV) on (a) calcined and (b) uncalcined

1789 LDHs (from Yang et al. 2005).

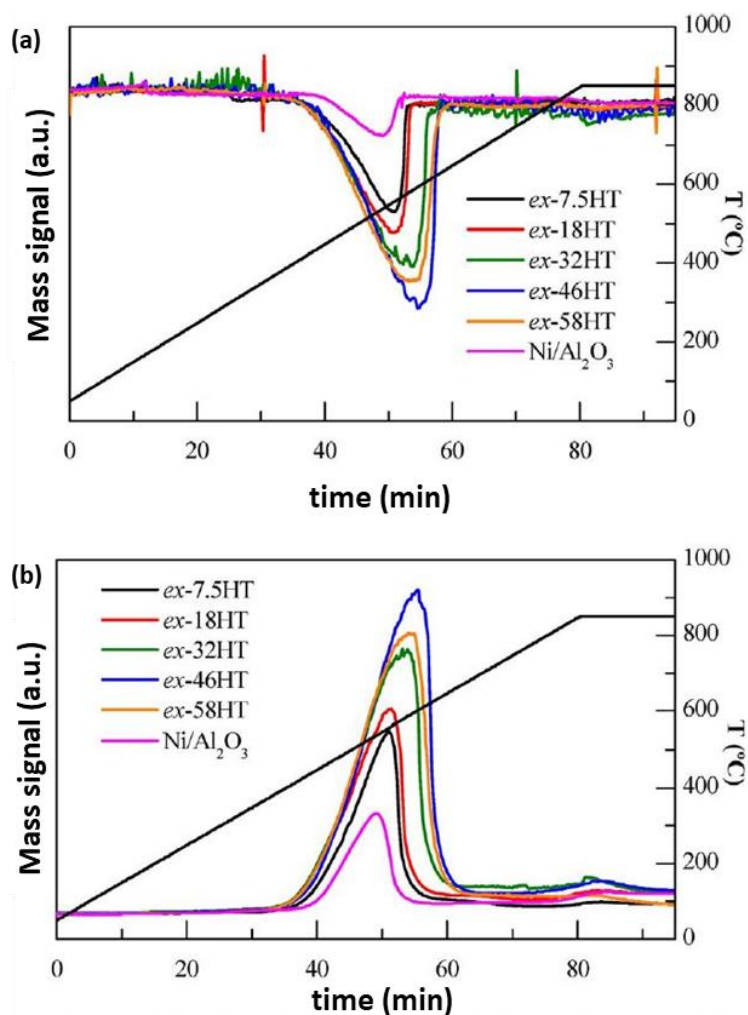


1790

1791 **Fig13.** Effect of contact time on percentage of dye removal Mg-Fe-CO<sub>3</sub>-LDH (from Ahmed  
 1792 and Gasser 2012).

1793 **Table 7.** Synthesis conditions of the LDHs and mixed oxides cited in the part “2.3.1.  
 1794 Hydrogen production”.

Reference	Type of material	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Synthesis method
Marquevich et al. 2001	Calcined NiAl hydrotalcite	104	Co-precipitation at high supersaturation, calcination at 400°C for 4h, then reduction under nitrogen steam at 600°C.
He et al. 2009, 2010	Co-NiMgAl hydrotalcite	uncalcined : 73 – 144 calcined : 103 – 180	Co-precipitation at high supersaturation and calcination at 600°C for 6h. The metal loading was fixed at 40% and the Co-Ni composition was varied from 40 to 0, 30-10, to 20-20, 10-30, and 0-40.
Cesar et al. 2016	NiMgAl hydrotalcite	–	Co-precipitation at low supersaturation and calcination at 750°C for 4h.
Halabi et al. 2012a, b	Calcined MgAl LDHs	15.6	Commercial hydrotalcite calcined at 400°C for 4h and loaded with K <sub>2</sub> CO <sub>3</sub> by dry impregnation method.
Chanburanasiri et al. 2013	MgAl LDHs	104	Commercial K <sub>2</sub> CO <sub>3</sub> -promoted hydrotalcite in cylindrical shape.
Ashok et al. 2008	Calcined NiCuAl LDHs	120 – 182	Co-precipitation at low supersaturation and calcination at 450°C for 5h. Atomic ratio between divalent (Ni <sup>2+</sup> + Cu <sup>2+</sup> ) and trivalent (Al <sup>3+</sup> ) cations varied from 2 to 9 but constant nickel metal content.
García-Sancho et al. 2017	Calcined NiMgAl LDHs	69 – 156	Co-precipitation at low supersaturation in presence of urea, and calcination at 850°C for 10h.
Sikander et al. 2018	Calcined NiMgAl LDHs	–	Co-precipitation at low supersaturation, and calcination at different temperatures: 550, 700, and 800°C for 6h.



1796

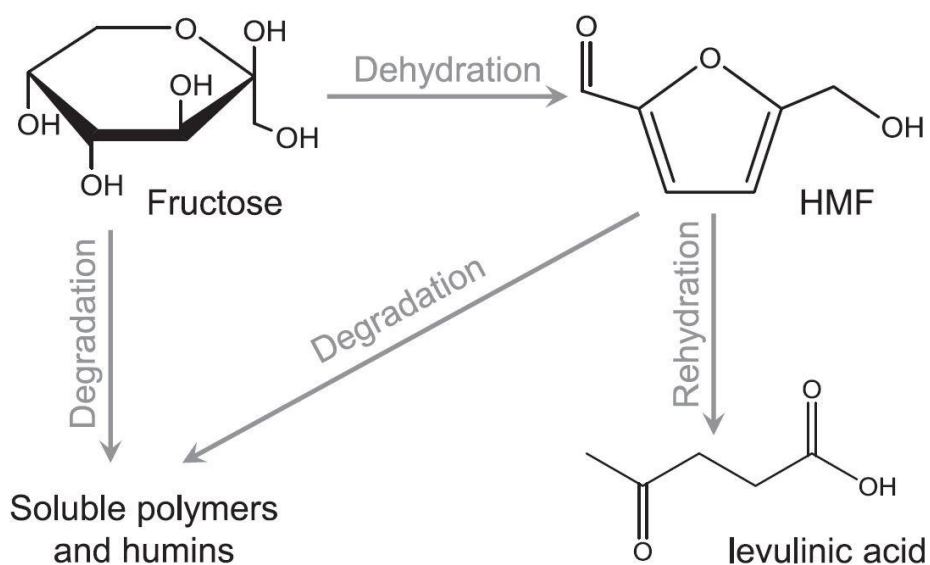
1797 **Fig14.** Temperature-programmed methane conversion (a) and hydrogen production (b) by  
 1798 nickel-containing calcined hydrotalcites (from García-Sancho et al. 2017).

1799

1800 **Table 8.** H<sub>2</sub> production by several types of hydrotalcite-based materials.

M(II)/M(III) molar ratio	Conversion (%)	Selectivity (%)	Synthesis method	Source	References
2	20 – 79.7	66.6 – 72.1	Co- precipitation	Sunflower oil	Marquevich et al. 2001
3	62	70	Co- precipitation	Ethanol	He et al. 2009

-	100	70	Co-precipitation	Ethanol	de Souza et al. 2012
1.56	72 – 99.6	91.3 – 99.8	Commercial	Methane	Halabi et al. 2012b
1	49 – 94	56.1 – 96.5	Co-precipitation	Ethylene glycol	Cesar et al. 2016
M(II)/M(III) molar ratio	Conversion (%)	H <sub>2</sub> produced (a.u.)	Synthesis method	Source	References
3	15 – 55	246 – 1253	Urea + co-precipitation	Methane	García-Sancho et al. 2017
3	15 – 40	250 – 1100	Urea + co-precipitation	Methane	García-Sancho et al. 2018



1801  
 1802 **Fig15.** Scheme of the reactions involved in fructose dehydration and the resulting formation  
 1803 of 5-HMF and byproducts (from Dou et al. 2018).

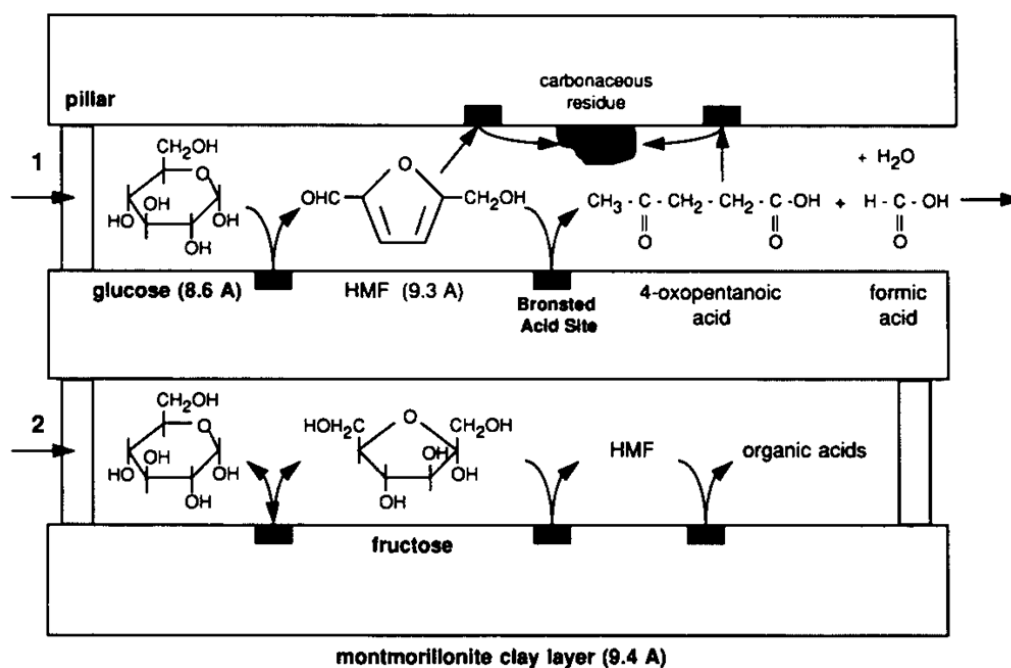
1804  
 1805 **Table 9.** Synthesis parameters of the lamellar materials cited in the part “2.3.2. 5-  
 1806 Hydroxymethylfurfural formation”.

Reference	Type of material	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Synthesis method
-----------	------------------	---	------------------

<b>Lourvanij and Rorrer 1994</b>	Pillared Na-montmorillonite	137.7 – 249.6	Na-montmorillonite mixed into the pillaring agent solution.
<b>Fang et al. 2014</b>	Cr-montmorillonite K10	–	K-10 montmorillonite exchanged with Cr cations.
<b>Chheda and Dumesic 2007</b>	Calcined MgAl LDH, MgO/ZrO <sub>2</sub> and MgO/TiO <sub>2</sub>	~ 300	MgAl LDH synthesized by <b>co-precipitation</b> at low supersaturation, and mixed oxides by sol-gel method. All these samples have been calcined at 450°C for 8h.
<b>Li et al. 2011</b>	Calcined NiMgAl LDH	34 – 117	<b>Co-precipitation</b> at low supersaturation with varying Ni at%, and calcination at 800°C for 5h.
<b>Zeng et al. 2009b</b>	Calcined AlZr LDHs	66 – 281	<b>Co-precipitation</b> at high supersaturation and calcination at 500°C for 6h.

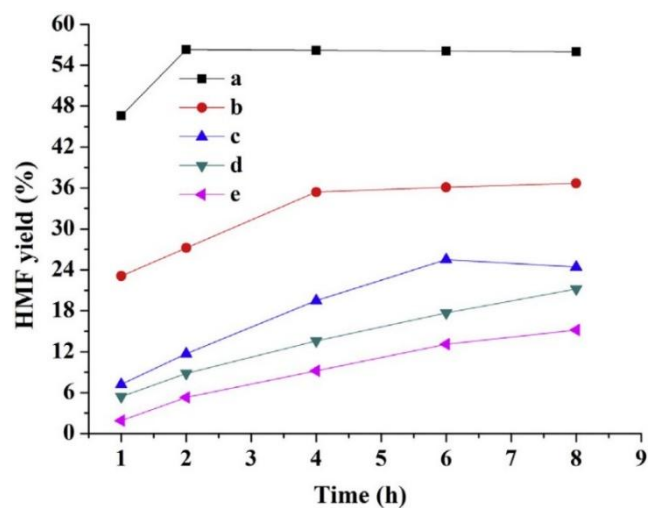
1807

1808



1809 **Fig16.** Proposed intraparticle diffusion and reaction scheme for glucose and fructose within a  
 1810 pillared clay catalyst. Reaction 1: sequential dehydration of glucose to HMF and organic acid.  
 1811 Reaction 2: isomerization of glucose to fructose. (from Lourvanij and Rorrer 1994).

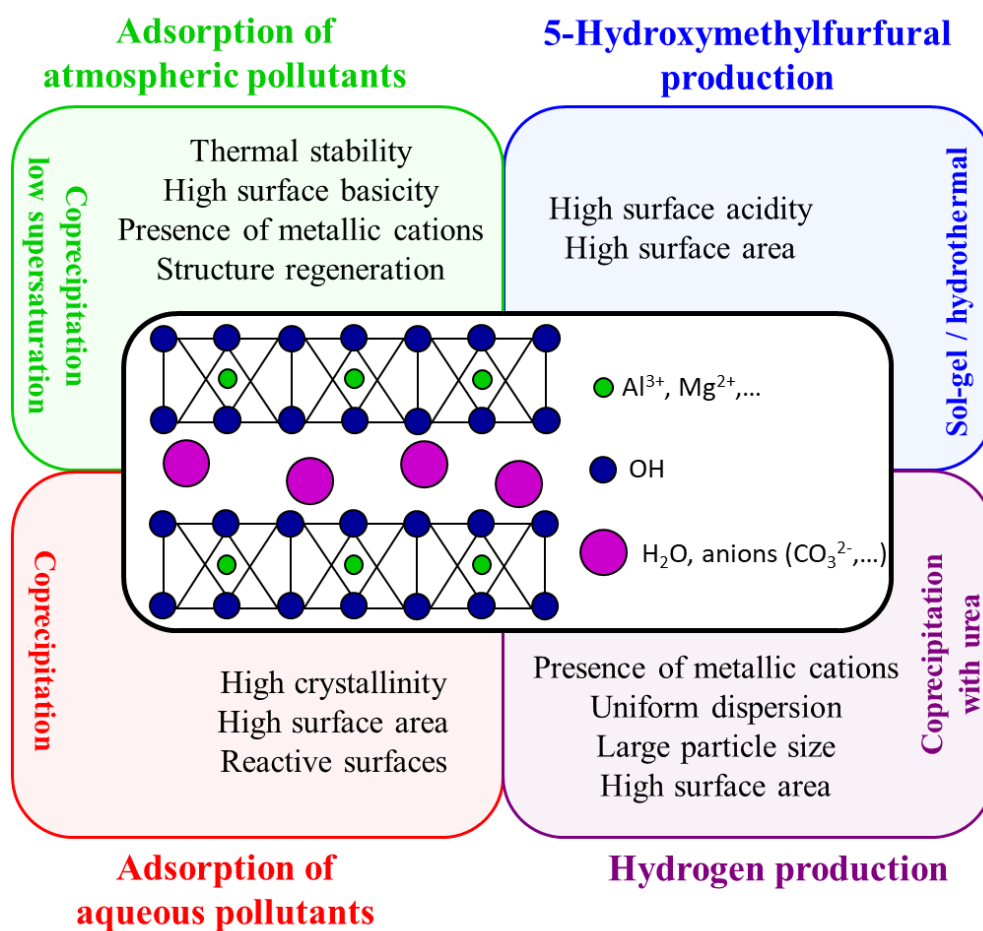




1812

1813 **Fig17.** Catalytic conversion of glucose into 5-HMF at various [BMIM]Cl concentrations in

1814 DMSO, e = DMSO only (from Fang et al. 2014).



1815

1816 **Fig18.** Relations between structural properties and applications of hydrotalcites and related  
 1817 materials.