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Research paper

# Some consequences of the fluorination of brucite-like layers in layered double hydroxides: Adsorption

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ABSTRACT

Hydrotalcite-like compounds were synthesised by co-precipitation method. The originality of the work is the replacement of structural $OH^-$ by $F^-$. Fluoride anions were incorporated as a part of the brucite like layers not as compensating anions. The resulting adsorptive properties of fluorinated materials are very different than those observed for the fluorine-free sample. The polarity and polarisability parameters were calculated by using dyes and xenon as molecular probes. The hydrogen bond accepting character and acido-basicity are the main properties enhanced because of the fluorination of hydrotalcite-like compounds, helping to diversify adsorption sites for chromophores or water.

## 1. Introduction

Layered double hydroxides (LDHs), commonly called hydrotalcite-like compounds (HTs), are a family of compounds currently used as catalysts, catalyst supports, adsorbents and ionic exchangers (Hattori, 1995; Laguna et al., 2007; Occelli et al., 2003; Perioli et al., 2011).

The versatility of LDHs is a consequence of their chemical structure that can be derived from a brucite structure ($Mg(OH)_2$), which is composed of linked octahedrons of magnesium hydroxide. The octahedrons form gibbsite-type sheets stacked in a hexagonal space group (Duan and Evans, 2006). In LDHs, a fraction of the divalent $Mg^{2+}$ ions is substituted by trivalent cations, *e.g.*, $Al^{3+}$. Because of this substitution, the hydroxide layers become positively charged but are charge-compensated by interlayer anions or anionic complexes. The composition of LDHs is described by the formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2][A^{n-}]_{x/n}.mH_2O$, where $M^{2+}$ and $M^{3+}$ are the di- and trivalent cations in the octahedral positions within the hydroxide layers. The value of x commonly ranges from 0.17 to 0.33. $A^{n-}$ represents an exchangeable interlayer anion that can vary. Although LDHs show the greatest affinity by carbonates, other anionic species can also intercalate into the space between the layers (Beaudot et al., 2004; Costantino et al., 1999; Miyata, 1975). The $M^{3+}$ and $M^{2+}$ ions are often $Al^{3+}$ and $Mg^{2+}$, respectively but may also be one of following: $Ga^{3+}$, $Cr^{3+}$, $Fe^{3+}$, $Ni^{2+}$, $Zn^{2+}$, and $Cu^{2+}$ among others.

Chemical composition variation is the best strategy to tune the acid–base properties of LDHs. In this sense, the nature of $M^{3+}$ and $M^{2+}$ has been widely explored (Cheng et al., 2011; Sampieri and Lima, 2009). However, the replacement of structural hydroxyl by fluoride was just reported last year (Lima et al., 2012). XRD and NMR results supported the replacement of blocks $(Al(OH)_6)^{3-}$ by $(AlF_6)^{3-}$. Fluorination of hydroxide layers changes significantly the physicochemical properties of LDHs; notably, the presence of fluoride diversifies the strength and number of acid–base pairs, as supported by qualitative and quantitative analyses of probe molecule adsorption, $CH_3NO_2$ (nitromethane) and $NH_3$ (ammonia), respectively.

The layered structure of LDHs collapses due to dehydration, dehydroxylation and anion loss when LDH is treated at temperatures between 200 and 400 °C. When this collapse occurs, mixed oxides are often obtained, which are commonly able to recover the layered structure when put in contact with water or an anionic aqueous solution. The collapse-recovery of the layered structure is frequently referred to as the "memory effect" (Pfeiffer et al., 2010; Stanimirova et al., 1999; Xu and Zeng, 2001). This effect is a property of the fluorine-free LDHs as well as of the fluorinated LDHs; obviously the presence of fluorine affects the cycle collapse-recovery of the layered structure. Particularly, during calcination, the coordination of $M^{3+}$ ions is partially lowered from octahedral to tetrahedral with the presence of fluorine enhancing the tetrahedral/octahedral ratio (Hibino and Tsunashima, 1998; Martínez-Ortiz et al., 2008). Therefore, the textural and structural properties of the fluorinated LDHs become different from those of the fluorine-free LDH. Thus, the goal of this work is to show some of the adsorptive properties of LDHs that are greatly influenced by the fluorination. The objective of many approaches is to determine the influence of fluorination on the hydrogen bond accepting character and on the acido-basicity of the mixed oxides. The modification of the nature of adsorption sites was on one hand probed by the modulation of adsorption

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of hydroxynaphthol blue (HNB) as pigment and $H_2O$ and $CO_2$ in gas phase. On the other hand, polarity and polarisability of the surface (Katritzky et al., 2004; Seifert et al., 2012; Zimmermann et al., 2002) were investigated by NMR *via* the adsorption of Xe and by UV–vis spectroscopy *via* the adsorption of a series of solvatochromic dyes.

## 2. Experimental procedure

### 2.1. Materials

Carbonate-containing Mg–Al LDHs with a Mg/Al molar ratio close to 3 were prepared by co-precipitation method at pH 10. A 1 M aqueous solution containing appropriate amounts of $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Na_3AlF_6$ (Aldrich, 99.99%, USA) was delivered into a reactor by a chromatographic pump at a constant flow of 1 $cm^3$/min. A second aqueous solution containing 2.0 M NaOH (Aldrich, 99%) plus 0.2 M $Na_2CO_3$ was simultaneously fed. The pH remained constant by controlling the addition of the alkaline solution using a pH-STAT Titrando apparatus (Metrohm, Switzerland). The suspension was stirred overnight at 80 °C, and then the solid was separated by centrifugation, rinsed thoroughly with distilled water, and dried overnight at 80 °C. The ratio of Mg/Al was maintained at 3 in the samples reported in this work. The source of aluminium was either aluminium nitrate or a mixture of aluminium nitrate with sodium hexafluoro-aluminate. A series varying the amount of fluorine was prepared. Table 1 summarises the composition of four samples under study.

### 2.2. Adsorption

Several molecules, polar or non polar, were adsorbed either from a gas or a liquid phase in order to show the different adsorptive properties of LDH with and without fluorine. Before the adsorption tests, the adsorbents were thermal treated at 400 °C for 8 h.

### 2.2.1. Dyes

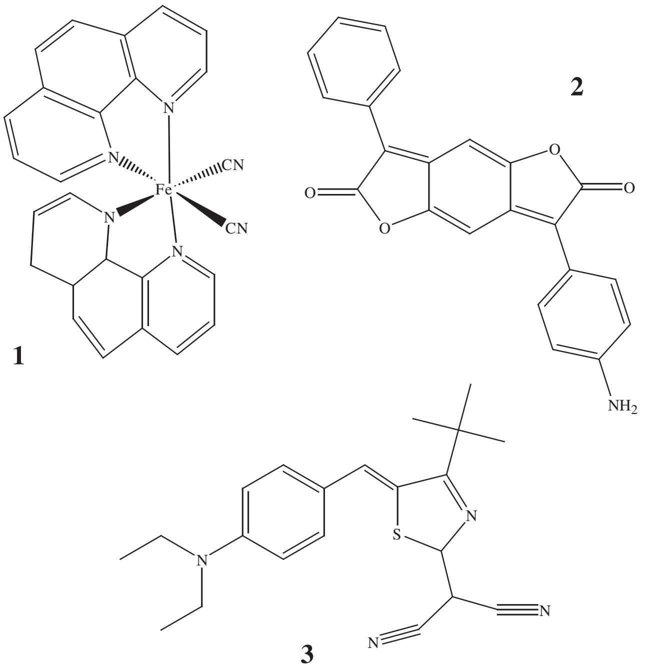
The following dyes were used with the purpose to evaluate the polarity parameters of mixed oxides emerged from thermal treatment of LDHs: dicyano-bis-(1,10-phenanthroline)-iron(II) complex (**1**); 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-b:4,5-b0]-difuran-2,6-dione (**2**) and 4-tert-butyl-2-(dicyano-methylene)-5-[4-(diethylamino) benzylidene]-Δ-thiazoline (**3**), Scheme 1. Adsorption of dyes was done according to the procedure followed earlier (Lungwitz and Spange, 2008; Spange et al., 2005). Briefly, dyes **2** and **3** were dissolved in cyclohexane, dye **1** was dissolved in dichloromethane. 5 mL of the dye solution per 0.1 g of the mixed oxide powder was used. The suspensions were shaken for 15 min under exclusion of light, decanted and dried under vacuum.

The evaluation of the polarity of samples was determined by monitoring solvent-dependent shifts of the UV/vis absorption band of a probe dye resulting from both rather specific (hydrogen bond donating (HBD) and hydrogen bond accepting (HBA)) and non-specific interactions (dipole–dipole, dipole–induced dipole, or London dispersion forces). In this sense, the multi-parameter approach of Kamlet–Taft was used to determine polarity of “white” oxide surfaces (Spange et al., 1999, 2001, 2005).

**Table 1**
Chemical composition of LDH samples synthesised by co-precipitation method.

| Code Sample | Chemical formula[a] | Mg/Al ratio | $d_{003}$ (Å)[b] |
|---|---|---|---|
| MA | $[Mg_{0.761}Al_{0.248}(OH)_2](CO_3)_{0.124}0.66H_2O$ | 3.06 | 8.31 |
| MAF-10 | $[Mg_{0.752}Al_{0.253}(OH)_{1.93}F_{0.07}](CO_3)_{0.126}0.58H_2O$ | 2.98 | 7.72 |
| MAF-25 | $[Mg_{0.738}Al_{0.242}(OH)_{1.73}F_{0.27}](CO_3)_{0.121}0.52H_2O$ | 3.04 | 7.59 |
| MAF-40 | $[Mg_{0.714}Al_{0.248}(OH)_{1.59}F_{0.41}](CO_3)_{0.124}0.49H_2O$ | 2.88 | 7.56 |

[a] As determined by chemical analysis.
[b] As determined by XRD (Lima et al., 2012.).



**Scheme 1.** Chemical structures of solvatochromic dyes.

The simplified Kamlet–Taft equation is the following:

$$\nu_{max} = \sim \nu_{max,0} + a\alpha + b\beta + s\pi^* \tag{1}$$

where $\sim \nu_{max,0}$ denotes the peak frequency value of a solvent reference system. The parameter α describes the HBD ability, β the HBA ability, and $\pi^*$ represents the dipolarity/polarisability. Further, a, b, and s are solvent-independent coefficients reflecting contributions of solvent effects to the UV/vis absorption shift $\nu_{max}$. α, β, and $\pi^*$ can be individually derived (Spange et al., 2005) from the UV/vis absorption maxima of the perichromic probe dyes **1**–**3** (Scheme 1).

$$\alpha = -7.49 + 0.46\nu_{max}(\mathbf{1})\left[10^{-3}cm^{-1}\right] \tag{2}$$

$$\beta = 3.84{-}0.20\nu_{max}(\mathbf{2})\left[10^{-3}\ cm^{-1}\right] \tag{3}$$

$$\pi^* = 9.475{-}0.54\nu_{max}(\mathbf{3})\left[10^{-3}\ cm^{-1}\right] \tag{4}$$

### 2.2.2. $H_2O$ and $CO_2$–$H_2O$ adsorption

Dynamic $H_2O$ and $CO_2$–water vapour sorption experiments were carried out on a temperature controlled thermobalance TA Instruments model Q5000SA, equipped with a humidity-controlled chamber, varying temperature, time, and relative humidity. All the experiments were carried out using around 3–5 mg of thermal treated LDH, distilled water, and CO2 (Praxair, grade 3.0) as carrier gas. The $CO_2$ flow used was 100 mL/min, and the RH percentages were controlled automatically with the Q5000SA equipment.

### 2.2.3. Xenon

For these experiments, the sample was placed in a NMR tube equipped with Young valves through which the xenon gas (Praxair, 99.999%) was equilibrated with the sample at 20 °C under different pressures. Prior to xenon loading, samples were dehydrated by gradual heating up to 400 °C under vacuum ($1.33 \times 10^{-4}$ kPa). The $^{129}$Xe NMR spectra were recorded at 20 °C using a Bruker Avance 400 spectrometer at 111.23 MHz. Single excitation pulses were used, and at least 2000