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Experimental (X-Ray Photoelectron Spectroscopy) and theoretical studies of benzene based organics intercalated into layered double hydroxide

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ABSTRACT

The present paper deals with a fine physico-chemical analysis of some hybrid materials combining an inorganic layered double hydroxide phase (LDH) with an organic benzene derivative entity R'-C_6H_4-R with R = $-SO_3^-$, $-CO_2^-$ and R′ = −H, −OH. The main topic of this work is, in a nanoscale, to propose a way to approach the understanding of the interactions between inorganic and organic sub-systems. The role of the anionic headgroup R is discussed in term of reactivity with the mineral support.

The classical expertise of materials *via* the PXRD technique puts into light an effective LDH interlayer space enlargement with the organics incorporation and a minimum angle of inclination for every organics within the LDH matrix. The originality of this study is to use the X-Ray Photoelectron spectroscopy (XPS) as a local probe of the chemical environments of the headgroup of the organic entities. In a parallel way, some quantum calculations (by using molecular and periodical codes) are carried out to best appreciate the electronic and structural evolutions before and after the intercalation step. A specific reactivity of the $-SO_3^-$ group compared with the $-CO_2^-$ one is evidenced. Moreover, a correlation at the first order is then set up between the net charges of atoms and the XPS binding energies of their core levels.

1. Introduction

In this paper, four benzene derivatives salts, the 4-hydroxybenzene sulfonate salt (shortly called HBS^-Na^+ salt), the benzene sulfonate salt (BS^-Na^+ salt), the 4-hydroxybenzoate acid salt (HBC^-Na^+ salt) and the benzoate acid salt (BC^-Na^+ salt), were intercalated into a hydrotalcite-type layered double hydroxide lattice $[Zn_{1-x}Al_x(OH)_2]^{x+}[X_{x/m}^{m-}.nH_2O]^{x-}$, represented as Zn_RAl LDH ($R = (1-x)/x$ for more clarity) with X = HBS, BS, HBC or BC.

Benzene sulfonate derivatives are important in some industrial processes and are used for example as intermediates in the production of chemicals such as azo dyes, optical brighteners, detergents [1] or as corrosion inhibitors [2]. The presence of these derivatives may lead to perturbations of the ecosystems. The use of anion exchange properties of LDHs and the adsorption capacity of the positively charged layers has been extended to the removal of organic pollutants as acid organic species for example. In the same scheme, benzoic acid derivatives are found in food and dye processing effluents [3,4] but can also be considered as a natural agent playing a major role in plant defense responses against pathogen attack [5]. For example, formation of 4-hydroxybenzoate can be elicited by treatment with pathogen fungal elicitors, as observed in various cultures [6]. In a hybrid materials context, the properties and applications of the LDH/acid organics systems have been the subject of a number of papers [7–10] but few papers report a study for the understanding of the interactions nature between the mineral support and the incorporated organic molecule. A comparison between two systems LDH/sulfonate derivatives prepared by a coprecipitation technique has been reported [11] and an estimation of the molecular orientation is obtained based on XRD data.

The aim of this work was then to investigate the sub-lattices interactions within four hybrid model systems, LDH-HBS, LDH-BS, LDH-HBC and LDH-BC hybrid materials through an experimental/theoretical coupled approach. In addition, the specific reactivity of each anionic group ($-SO_3^-$ for HBS^- and BS^-; $-CO_2^-$ for HBC^- and BC^-) with the host matrix has been investigated. Note that BS^- and BC^- present a unique functional group and their respective study would allow to estimate the role of the OH group for the two other bi-substituted benzene derivatives (HBS^- and HBC^-). Beside the

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use of the powder X-Ray Diffraction (PXRD), to monitor the structural evolution during the intercalation process, an original survey was achieved *via* the X-Ray Photoelectron Spectroscopy (XPS) to probe the electronic and chemical evolutions between the two subsystems (the mineral support and the organic entities). The comparison of some XPS data with quantum calculations was afterwards carried out to better understand the nature of the interactions. The different precursors of the hybrid materials, ie the layered inorganic matrix and the salts, have been first investigated to make an inventory of their physico-chemical specificities; the composite materials and the nature of resulting interactions were then studied on the basis of these initial experimental and theoretical data.

2. Experimental section and computational details

2.1. Materials: LDH and LDH-derivatives materials

The hybrid materials, with a general formula $[Zn_{1-x}Al_{x}(OH)_2]^{x+}[X_{x/m}{}^{m-}.nH_2O]^{x-}$ with $x = M^{III}/(M^{II} + M^{III})$ ($x = 0.33$) and X = HBS, BS, HBC or BC, have been synthesized by the standard coprecipitation method [12,13]. The choice of the composition, $x = 0.33$, among different prepared materials was done in view of the better crystalline degree recorded for this type of sample by comparison with the other matrix compositions, $x = 0.25$ and $x = 0.2$ [14].

These samples were obtained by the coprecipitation of zinc chloride hexahydrate (Acros organics reagent, 98% pure), aluminium chloride hexahydrate (Acros organics reagent, 99+% pure) and sodium salts. The sodium salts $HBS^{-}Na^{+}$ [sodium 4-hydroxybenzene sulfonate dehydrate, (Aldrich, CAS: 10580-19-5)], $BS^{-}Na^{+}$ [sodium benzene sulfonate, (Aldrich, CAS: 515-42-4)], $HBC^{-}Na^{+}$ [sodium 4-hydroxybenzoate, (Acros organics, CAS: 114-63-6)] and $BC^{-}Na^{+}$ [sodium benzoate, (Acros organics, CAS: 532-32-1)] have been used for intercalation. A mixture, of $ZnCl_2.6H_2O$ and $AlCl_3.6H_2O$ was then dissolved in 200 ml of deionised water to obtain a Zn_2Al-Cl solution (1 M). The aqueous solution was slowly added (0.013 mL/min) under magnetic stirring and nitrogen flux to 100 mL of X solution (0.1 M) at room temperature with X the sodium salt. Experimental conditions of pH were continuously maintained to an 8.5 ± 0.2 value for all mixtures with a controlled addition of NaOH solution (1 M) to ensure the correct building of the host LDH phase. The resulting suspensions were stirring for 24 h under nitrogen flux at 70 °C for LDH-HBS hybrid phase and for 22h at 20 °C for the other samples. The final products were afterwards filtered, washed with distilled water and kept in a drier at 80 °C during 48 h.

For more convenience and clarity, inorganic matrix and hybrid phases have been so labeled, according their chemical composition: Zn_2Al-Cl, Zn_2Al-HBS, Zn_2Al-BS, Zn_2Al-HBC and Zn_2Al-BC.

2.2. Analytical techniques

2.2.1. Powder X-Ray diffraction (PXRD)

After their preparation, all the samples have been systematically analysed by the PXRD to monitor the qualitative phase composition, the crystalline state and possible structural changes after organics incorporation.

PXRD patterns were obtained with an X-Pert Pro X-Ray diffractometer using a CuK_{α} radiation (1.5418 Å) equipped with a graphite back-end monochromator and an Argon-filled proportional counter. During data collection, the sample holder was rotating at the speed of 30 revolutions per min. Measurements conditions were: diffraction interval $2° < 2\theta < 70°$, step size $\Delta(2\theta) = 0.04°$ and counting time per step 20 s.

All the powder patterns were analysed by the Rietveld method by using the *Fullprof.2k* Program [15] to extract structural and microstructural parameters. The hybrid LDH phase was refined by using the Profile Matching mode (because no structural model were available for these hybrid compounds) with the hydrotalcite $R\overline{3}m$ symmetry usually used to describe the Zn_2Al LDH phases in agreement with powder patterns recorded.

2.2.2. X-Ray Photoelectron Spectroscopy (XPS)

XPS analyses were performed on a Kratos Axis Ultra 165 spectrometer which employed a magnetic immersion lens to increase the solid angle of photoelectrons collection from small analysis areas to minimise the aberrations of the electron optics. A monochromatic and focused (spot dimensions of 700 μm by 300 μm) Al K_{α} radiation (1486.6 eV) was operated at 450 W under a residual pressure of 2×10^{-9} mbar. The spectrometer was calibrated using the photoemission lines of Au ($Au4f_{7/2} = 83.9$ eV, with reference to the Fermi level) and Cu ($Cu2p_{3/2} = 932.5$ eV); for the $Au4f_{7/2}$ line, the full width at half maximum (FWHM) was 0.86 eV in the recording conditions. Charge effects were compensated by the use of a charge neutralisation system (low energy electrons [typically 1.85 eV]) which had the unique ability to provide consistent charge compensation. All the neutraliser parameters remained constant during analysis. Peaks were then shifted to align adventitious hydrocarbon C1s photoemission to a 284.6 eV binding energy. High-resolution regions were acquired at constant pass energy of 40 eV. All the samples were grinded prior to analysis to avoid effects due to the surface texture. Short acquisition time spectra were recorded before and after each normal experiment to check that the samples did not suffer from degradation during the measurements. The XPS signals were analysed by using a least squares algorithm and a non-linear baseline. The fitting peaks of the experimental curves were defined by a combination of Gaussian (70%) and Lorentzian (30%) distributions. Quantification was performed on the basis of Scofield's relative sensitivity factors [16].

2.3. Computational details

The electronic structures of the $HBS^{-}Na^{+}$ and $HBC^{-}Na^{+}$ salts were performed using the periodic LCAO-B3LYP approach developed in the periodic *ab initio* CRYSTAL06 code [17], and by referring to the crystallographic data from the literature [18,19]. The crystalline orbitals are expanded in terms of localized atomic Gaussian basis set, in a way close to the LCAO (linear combination of atomic orbitals) method currently adopted for molecules. The eigenvalues equations are solved for the B3LYP functional using the Becke's exchange [20] and Lee-Yang-Parr's correlation functional [21]. All electrons basis set have been adopted: 8-41G* for oxygen [22], 6-21G* for carbon [23], 86-311G* for sulphur [24], 8-511G for sodium [25], 2-11G* for hydrogen [26], 8-31G for aluminium [27] and 86-411d4G for zinc [28] In optimizing the geometry, we allowed the relaxation of all atoms, cell parameters and the fractional atomic coordinates.

For studying the organics geometry and the sub-lattices interactions, a molecular model approach using the GAUSSIAN03 package [29] was considered (basis set: 6-311G* [30]) by interfering a mineral cluster $Al(OH)_3$ (representing the active part of the LDH layers and which geometry was deducted from a periodical approach -see Section 4-) with the organic molecule. Remind that the LDH layers are positively charged due to the partial substitution of some zinc (II) atoms by some aluminium (III) ones. This allows to consider the aluminium atoms as positive centers which will be in direct interaction with the organic fragment (HBS^{-}, BS^{-}, HBC^{-} and BC^{-}).