Intercalation and grafting of benzene derivatives into zinc–aluminum and copper–chromium layered double hydroxide hosts: an XPS monitoring study†

Solenne Fleutot,a Jean-Charles Dupin,a* G. Renaudinb and Hervé Martineza

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We report an original strategy to describe, via X-ray photoelectron spectroscopy (XPS) measurements, the interactions between the organic and the mineral sub-systems within a multifunctional hybrid material. A tunable layered double hydroxide (LDH) host system, either a Zn2Al- or Cu2Cr-hydrotalcite like compound, is modified with the insertion of the organic guest entities, 4-phenol-sulfonate (HBS) or -carboxylate (HBC). The resulting interactions are studied at two levels: after the organic molecules’ insertion in the host LDH (ionic exchange between the LDH counter-ions and the organic anions) and after the condensation (grafting) of the organic species onto the mineral layers when thermally treated. For the inserted material, the main XPS results show a stabilization of the organic molecules within the mineral sheets via H bonding as found elsewhere with FTIR study, the mineral matrix being unchanged. The XPS signal of the organic molecules slightly changes with a widening of core peaks, attesting to some local surrounding modifications. When heating up the Zn2Al hybrid material, stronger interactions between organic and inorganic systems appeared from around 80 °C with some obvious electronic changes as monitored with the XPS S2p signal of the HBS guest molecules. At the same time, the PXRD pattern clearly shows a decrease of the basal spacing according to a two step contraction process which could be interpreted as a progressive organic molecule condensation onto the inorganic layers via iono-covalent bonds. A copper-chromium LDH is also studied to probe the same kind of interactions with the HBS molecules. The ability of distortion of such mineral material involves a peculiar process of contraction from 40 °C with the immediate and effective anchorage of organic molecules.

1 Introduction

For several years, hybrid materials have been of great interest considering their structural characteristics and potential applications they are associated with due to their specific chemical activities. The family of layered double hydroxides (LDH) [MII1−xM0x(OH)2]x+[A−nH2O][MII−R−M0−X] with R = 1 – x/2, represents a class of open systems for different types of reactive molecules that can offer the possibility to build a large set of multifunctional organic hybrid systems [e.g., ref. 2–8]. Application areas for hybrid systems revolve around their physical properties (e.g., mechanical behavior) but even expand over to novel materials dedicated to separation, inert filler, electrolytes, and catalytic processes.

Most articles concerned with LDHs generally deal with their ion exchange ability but few studies investigate extensively the potential of LDH-based pillared materials resulting from organic–inorganic bondings. Actually, these studies usually focus on the only evidence of the grafting event with thermogravimetry or FTIR measurements and no specific attention is paid elsewhere. Prevot et al. reported that a heat treatment of Cu2Cr–PPA over 100 °C resulted in a reduction of the LDH interlayer space and the permanent grafting of the PPA units to the layers. Two types of grafting on layered structures are usually reported in the literature with, for example, the topotactic ionic exchange of pending groups or the direct condensation of adsorbed or intercalated molecules with oxychloride or hydroxyl layers. Concerning the grafting of organic molecules onto hydroxide layered structures, most of the studies focused on kaolinite, boehmite or basic metal salts interfering with alcohol molecules or their derivatives. Nevertheless, a decade ago, C. Forano et al. were even aware of the interest of such tunable pillared materials and a detailed study of various organics incorporated into
ZnAl- and CuCr-hydragrotalite-like compounds was performed in order to investigate their reactivity toward the grafting under thermal treatment. Shrinkage of host material interlayer spacing was assigned to the OH interactions with the guest organic molecules, the anchorage being deduced on the basis of FTIR spectra modifications (e.g. for new typical Al–O–C vibration modes). C. Sanchez extended the definition of hybrid materials to the direct knowledge of the possible interactions between the inorganic and organic species. Class I hybrid materials are described with weak interactions (e.g., van der Waals, hydrogen bonding or weak electrostatic interferences) whereas Class II hybrid materials have strong chemical links between the components and afford stabilized configurations with new properties. Even if the grafting process can technically be monitored with a combined PXRD-FTIR-TG analysis, we are still trying to better understand the chemical link between inorganic/organic subsystems.

The aim of the present work is to improve the description of such hybrid LDH based systems at the atomic scale. In the following, X-Ray Photoelectron Spectroscopy (XPS) is used as a new investigative tool to emphasize the evolution of interactions between some organic molecules (phenol benzene sulfonate (HBS) or carboxylate (HBC)) and $\text{M}^{\text{II}}$-$\text{M}^{\text{III}}$-hydragrotalite like networks ($\text{M}^{\text{II}} = \text{Zn}^{2+}, \text{Cu}^{2+}$ and $\text{M}^{\text{III}} = \text{Al}^{3+}, \text{Cr}^{3+}$) as previously initiated. The interest of such organic molecules lies in their industrial use as chemical intermediates for dye synthesis, pharmaceutical production or detergent preparation. They are also active agents in the healing properties of some plants. However, an excessive amount of these molecules in the nature would have a deep and noxious impact on ecosystems. Some first possibilities have been demonstrated to collect unusable wastes onto LDH absorbent supports. Moreover, these molecules differ in their functional group ($\text{SO}_3^{\text{a}}$ or $\text{CO}_2^{\text{a}}$ with respective acidity constants, $\text{p}K_{\text{a}}$, of −2.19 and 4.08 and their specific conformation (planar and rigid for HBC, bended and flexible for HBS). X-Ray Photoelectron Spectroscopy (XPS) has a special place among surface analytical techniques because of its ability to acquire nondestructively direct information of atom electronic states. In addition, the technique provides quantitative analysis of solid surfaces which is of significant fundamental and practical importance in understanding materials behavior. The chemical state information is commonly derived from precise measurements of photoelectron energies, and to an increasing extent, from measurements of Auger electron lines, generally more sensitive to even slight electronic changes. Chemical shifts in X-ray excited Auger lines are usually larger than those of the photoelectron lines. Among various analytical ways of materials characterization, XPS has also demonstrated it could afford significant information for open-shell paramagnetic metal analogues through the evolution of the Auger parameter ($\text{z'}$) or the intensity of satellite secondary structures. In the XPS study, the Auger parameter ($\text{z'}$) is conventionally defined as the sum of the kinetic energy ($\text{KE}$) of the most prominent and sharp core−core Auger transition and the binding energy (BE) of the most prominent and sharp core−ionization peak. The Auger parameter has been applied as an empirical tool to identify chemical states of the elements in cases where charging or small shifts in core binding energies does not allow an adequate characterization of the sample. For metals with a high number of electrons, actual chemical effects are often weak, hidden or hard to interpret. As mostly one or two valence levels are involved in the emission of the Auger electron, a careful analysis of the Auger lines could then allow one to reveal the changes in the levels’ electron densities due to a change in the chemical environment. In the case of the studied host matrix (Zn$_2$Al-LDH, Cu$_2$Cr-LDH), a change in the crystallographic symmetry and a lowering of coordination around the metal atoms can be envisaged. The crystal field geometry around the metal cation could presumably be involved in the interferences between organic and inorganic sub-lattices. Different potentialities of the XPS, final-state effects such as multiplet splitting and shake-up secondary peaks are considered for identifying the chemical environments’ evolution and in order to envisage new original routes for understanding phenomena at the nanoscale. Organic anions with a rigid molecular structure (HBC) are compared to more flexible ones (HBS) in order to precisely determine their potentialities for stabilizing the extended mineral matrix after the insertion. Some first theoretical calculations were carried out for supporting the discussion about organics stabilization within the mineral host network. The condensation ability of HBS anions is finally investigated in two different LDH networks to appreciate the precise behavior of the host matrix.

## 2 Materials and methods

### 2.1 Preparation of hybrid samples

Hybrid materials, with the general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_{x}(\text{OH})_2]^y\times[\text{A}^-_{x}n\text{H}_2\text{O}]$ ($\text{M}^{\text{II}} = \text{Zn or Cu}, \text{M}^{\text{III}} = \text{Al} or \text{Cr})$ with $\text{A}^- = \text{HBS or HBC}$ and $x = \text{M}^{\text{III}}/(\text{M}^{\text{II}} + \text{M}^{\text{III}})$ ($x = 0.33$), have been synthesized by the standard coprecipitation method. The $\text{Zn}_2\text{Al}$ based hybrid samples were obtained by the co-precipitation of zinc chloride hexahydrate (Acros Organics, 98% pure), aluminum chloride hexahydrate (Acros Organics, >99% pure) or sodium 4-phenol carboxylate dihydrate (HBC) (Sigma-Aldrich, 98% pure) and sodium 4-phenol sulfonate dihydrate (HBS) (Sigma-Aldrich, 98% pure) or sodium 4-phenol carboxylate dihydrate (HBC) (Acros Organics, 99% pure) as described in ref. 16. The $\text{Cl}^-$ counter-ion has been chosen for the study as it exchanges more easily than carbonates which are more reactive with the LDH like matrix.

For hybrid Cu$_2$Cr–LDH phases, preparations were also conducted with the coprecipitation method at room temperature, with a molar excess of the organic anions (HBS) of 10 with regards to the required amount for a stoichiometric counter ion exchange. The pH was adjusted to 5.0 when blending (3 mL min$^{-1}$) 150 mL solution of 0.25 M Cu(NO$_3$)$_2$·3H$_2$O (Sigma-Aldrich, puriss. p.a., 99–104%) and 0.125 M of Cr(NO$_3$)$_3$·9H$_2$O (Sigma-Aldrich organics reagent, 98% pure) with the HBS salt. The Cu$_2$Cr–HBS phase was then centrifuged in non-carbonated water and dried at room temperature during 72 h.

Some $[\text{Zn}_{1-x}\text{Al}(\text{OH})_2]^y\times[\text{Cl}^-_{x}n\text{H}_2\text{O}]$ or $[\text{Cu}_{1-x}\text{Cr}(\text{OH})_2]^y\times[[\text{NO}_3^-_{x}]_{x}n\text{H}_2\text{O}]$ ($x = 0.33$) precursors were also prepared...
under quite similar conditions (pH = 8.0 for Zn$_2$Al–Cl, pH = 5.5 for Cu$_2$Cr–NO$_3$) in order to get some initial reference data. Finally, for more clarity, materials are labeled Zn$_2$Al–Cl, Cu$_2$Cr–NO$_3$ for reference host matrix and Zn$_2$Al–HBS, Zn$_2$Al–HBC and Cu$_2$Cr–HBS for hybrid materials.

2.2 Thermal treatments

Grafting of intercalated organic anions was activated by thermal treatments of the hybrid compounds in a tubular oven. A 50 mg sample was submitted to progressive heating in a 20–300 °C range in air, during 12 h. Samples were kept in the oven in sealed air tight tubes for 24 h which afterwards have been opened up in a continuously purified nitrogen atmosphere glove box with low rates of O$_2$ and H$_2$O (around 5 ppm for both), directly connected with the X-ray photoelectron spectrometer. This precaution to keep wet surroundings is necessary to avoid the dehydrated LDH readsoorbing water while cooling down and then expanding a little bit. Same thermal treatments were carried out in situ in the PXRD spectrometer with simultaneous monitoring.

3 Characterization

Powder X-ray diffraction (PXRD)

After the preparation, all the samples were systematically analyzed by the PXRD technique to monitor the phase composition, the crystalline state and the possible structural changes after organics incorporation. PXRD patterns were obtained with an X-Pert Pro X-ray diffractometer using Cu-K$_\alpha$ 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 a speed of 30 revolutions per minute. Powder patterns were first recorded at room temperature for the LDH-precursor and the Zn$_2$Al-, Cu$_2$Cr-hybrid materials and afterwards, an in situ thermal acquisition was achieved on the hybrid material from room temperature up to 1000 °C. Measurements conditions were: diffraction interval 2° < 2θ < 105° (patterns are represented in the papers in a 2–70° range and 4–38° range in Fig. 1 and 5 respectively), step size Δ(2θ) = 0.04° and 0.08° for room temperature and thermal acquisition respectively; counting time per step 20 s and 4 s for room temperature and thermal acquisition respectively. All the powder patterns were analysed by the Rietveld method by using the Fullprof.2k Program$^{25}$ to extract refined structural and microstructural parameters.

X-Ray photoelectron spectroscopy (XPS)

XPS analyses were performed on a Thermo K-Alpha photoelectron spectrometer. A monochromatic and focused (spot dimensions of 400 μm) Al K$_\alpha$ radiation (1486.6 eV) was operated at 120 W under a residual pressure of 6 × 10$^{-9}$ mbar. The spectrometer was calibrated using the photo-emission 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. High resolution regions were acquired at a constant pass energy of 40 eV. 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. All the samples were ground prior to analysis to avoid effects due to the surface texture. For the hybrids study, charge referencing

Fig. 1  SEM images of (a) LDH host Zn$_2$Al–Cl and (b) LDH host Cu$_2$Cr–NO$_3$, (c) hybrid Zn$_2$Al–HBS, (d) hybrid Zn$_2$Al–HBC and (e) hybrid Cu$_2$Cr–HBS.
was done against adventitious carbon (C1s binding energy = 284.6 eV). Due to the type of samples (powders), a conductive carbon double sided tape has been used on the sample holder. Spectra were analyzed and mathematically fitted using CasaXPS software.26

Electron microscopy

Morphological characterization of the samples was carried out using a Cambridge Stereoscan 360 field emission gun (FEG) scanning electron microscope operating at 3000 eV at a 5 mm working distance. Samples were prepared by dispersion of fine ground material onto a carbon film supported on a Cu grid. To improve the conductive performances, samples were metalized by gold coating.

FTIR analysis

Attenuated Total Reflectance Fourier Transform infrared (FT-IR) spectra were measured in the range 400–4000 cm−1 on a FTIR Nicolet 5700 (Thermo Electron Corporation) spectrometer equipped with a Smart Orbit accessory.

Computational details

For studying the organics geometry and the sub-lattice interactions, a molecular model approach using the GAUSSIAN03 package27 was considered (basis set: 6-311G*) by interacting a mineral cluster Al(OH)3 (representing the active part of the LDH layers) and which geometry was deduced from a periodical approach—see section 4 with the organic molecule. Full details are given in ref. 16.

4 Results and discussion

4.1 Precursors characterization

4.1.1 LDH host materials. The SEM image of the Zn2Al–Cl LDH host (Fig. 1a) evidences a platelet morphology as commonly seen for hydrotalcite type materials28 but the coprecipitation method of synthesis does not allow one to reach well-faceted crystallites with the expected octahedral symmetry. Data obtained for the Cu2Cr–NO3 system (Fig. 1b) show some smaller particles without a certain morphology which is concomitant with the expected non-planar surface of the material. Crystallinity of Zn2Al–Cl would be better than Cu2Cr–NO3 one which attests to some initial peculiarities between host systems. For the hydroxide zinc–aluminum preparation, the pH range seems more suitable for formation of the hydrotalcite phase.

The X-ray diffraction pattern of the powder precipitated from the zinc and aluminium salts solution confirmed the formation of the desired hydrotalcite-like zinc aluminium hydroxide chloride, Zn2Al(OH)2Cl2·2H2O (JCPDS file n° 38-0487), with a basal spacing (d003 = c/3) of 7.72 Å (Fig. 2a, Table 1). The calculated lattice parameter a = 3.0713(2) Å is related to the metal–metal distance through the a = 2 × d111 relation and is in good agreement with the experimental Zn2+/Al3+ molar ratio of 2. The Cl− ions occupy a 2.942 Å interlayer space considering the mean thickness of a LDH layer (~4.780 Å).30,31

For Cu2Cr–NO3, the XRD pattern is not well-resolved and noisy (Fig. 2d). Despite the presence of the monochromator on the spectrometer, a residual fluorescence ray could partially contribute to such an intense background signal. Like Zn2Al–Cl, the diffraction lines are indexed in the R3m space group, usually found for LDH phases in which the two Cu2+, Cr3+ cations are in the same 3a crystallographic sites. The a parameter is 3.0400 Å and the basal spacing can be estimated to 9.07 Å. The average Cu2Cr–NO3 layer thickness is similar (~4.780 Å) to the Zn2Al–Cl system. Some EXAFS and XANES studies of layered double hydroxides report some precise details of these structural parameters.32

For the LDH matrix, chloride or nitrate precursors can be equally used for exchange with organic molecules as referred to by I. Y. Park et al.33 in a work dealing with indigo carmin insertion within a MgAl system. Considering the cations’ radii (0.730 Å for Cu2+, 0.700 Å for Zn2+, 0.620 Å for Cr3+ and 0.535 Å for Al3+), the Cu2Cr–LDH unit cell in the (a,b) plane would be the most important but the a parameter is lower than for Zn2Al–LDH. The observed decrease could be attributed to the M(OH)6 octahedron distortion under the Jahn–Teller effect commonly reported for copper divalent derived structures. In 2000, Roussel et al.32b reported a study about cationic order and structure of a Cu2Cr LDH system in which some EXAFS data have predicted different M–O distances into coordination octahedrons for Cu2+ and Cr3+. The pseudo-octahedral environment around copper atoms is described with four oxygen atoms at 1.98 Å (equatorial position) from the metallic center, the last two ones (axial positions) having a distance of 2.30 Å, in agreement with the distortion effect evoked. As reported in Hofmeister’s work,34 for an ideal Cu2+Cr3+ = 2 stoichiometry, divalent copper cations are finally surrounded in the cationic plane by 3 copper atoms and 3 chromium atoms; trivalent chromium atoms being surrounded by 6 copper atoms. In this model, the unit cell a

Fig. 2 PXRD patterns of: (a) Zn2Al–Cl, (b) hybrid Zn2Al–HBS, (c) hybrid Zn2Al–HBC, (d) Cu2Cr–NO3, and (e) Cu2Cr–HBS.
The local arrangement around 3d copper atoms corresponds to an octahedral distortion related to the Jahn–Teller effect. This phenomenon involves the decrease of the $a$ parameter. Considering 3d orbitals ($t_{2g}$, $e_g$), the decrease of the symmetry would allow one to split the degeneracy and to enhance the partially occupied d orbitals stability. In the case of an octahedral site, a partially full d level’s configuration (e.g., $Cu^{2+}$, $4s^0 3d^9$), will affect particularly the $e_g$ orbitals with a more pronounced polyhedral distortion associated with the $s^*$ character of these orbitals. The degeneracy splitting would then lead ligands to get closer in the $xy$ plane but would favor those in the $z$ direction to keep away from each other, as mentioned in an EXAFS simulation study of Roussel. Then, the arrangement of copper distorted octahedrons with those, more regular and well-shaped, of chromium, leads to a series of layer portions in different planes, then involving a surface microrugosity.

The XPS examination of the Zn$_2$Al–Cl LDH and Cu$_2$Cr–NO$_3$ LDH host materials led to the characterization of well-defined hydroxide environments as the Zn3p$_{3/2}$ and Al2p binding energies were respectively recorded as 89.6 eV and 75.0 eV (Fig. 3a,b, Table 2); those of Cu2p$_{3/2}$ and Cr2p$_{3/2}$ being located at 934.4 eV (accompanied with two characteristic satellites peaks) and 577.0 eV (Fig. 4a and b, Table 2) in agreement with the literature. The atomic ratios of Zn/Al and Cu/Cr have been respectively estimated at 2.19 and 4.00. The values for copper–chromium systems strongly differs from the expected one of 2 probably due to: the photoionization sensitivity factors which are difficult to estimate for some transition metals—the lineshape background (in the present work; the traditional Shirley background was used as done in most of the papers), and to the possible precipitation of a minor amorphous Cu(OH)$_2$ phase. As seen previously, in the case of the copper systems, as for open-shell paramagnetic metal analogues, it is often usual to consider some discussions on the basis of the apparent Auger parameter $\alpha'$ ($=BE(Cu2p_{3/2}) + KE(Cu_L3M4,5M4,5))$ and the ratio of the relative areas of satellite peaks over the main ionization peak (Isat/Imain). The position and intensity of the satellites peaks are important for best understanding the

### Table 1

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<th>Compound</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$d$ gallery height (Å)</th>
<th>Space group</th>
<th>Average apparent crystallite size (nm)</th>
<th>Average apparent crystallite size with anisotropy (nm)</th>
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<td>60 ± 10</td>
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<td>10 ± 5</td>
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![Fig. 3](image-url) XPS core levels: Zn3p of (a) Zn$_2$Al–Cl, (c) Zn$_2$Al–HBS RT; (e) Zn$_2$Al–HBS at 200 °C, Al2p of (b) Zn$_2$Al–Cl, (d) Zn$_2$Al–HBS RT; (f) Zn$_2$Al–HBS at 200 °C.
Table 2  XPS composition table of organic molecules (HBS-Na\(^{+}\), HBC-Na\(^{+}\)), host materials (Zn\(_2\)Al–Cl LDH, Cu\(_2\)Cr–NO\(_3\) LDH) and derivative hybrid systems at different temperatures. Binding energies and full width at half maximum (in parentheses) are reported in eV and atomic percentages.

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<th>HBC-Na(^{+})</th>
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<th>Zn(_2)Al–HBS 200 °C</th>
<th>Cu(_2)Cr–NO(_3)</th>
<th>Cu(_2)Cr–HBS 40 °C</th>
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<td>74.6 (1.5)</td>
<td>74.6 (1.5)</td>
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copper atoms electronic structure. In spinel materials for example,\textsuperscript{45} intensity of copper core levels satellites peaks are higher for copper-chromium and copper–rhodium families and depends on the coordination octahedron deformation of the cupric ion. In these conditions, all previous but even additional data are useful when the main core peaks survey is not suitable enough to determine precise metal oxidation state changes and coordination symmetry. The kinetic energy of Cu\textsubscript{L3M4,5M4,5} was deduced from the XPS analysis and used for systematically calculating the corresponding Auger parameter (see Fig. ESI1 in the ESI)\textsuperscript{w}.

For the Cu\textsubscript{2}Cr–NO\textsubscript{3} LDH host material, \( \alpha' \) was calculated to 1851.0 eV and \( I_{\text{sat}}/I_{\text{main}} \) was estimated to be 0.77 which corresponds to non-regular octahedral coordination of copper centers\textsuperscript{43} different from classical Cu(OH)\textsubscript{2} (\( \alpha' = 1851.8 \) eV, \( I_{\text{sat}}/I_{\text{main}} = 0.68 \)) or Cu(NO\textsubscript{3})\textsubscript{2} (\( \alpha' = 1850.3 \) eV, \( I_{\text{sat}}/I_{\text{main}} = 0.81 \)) environments. In the LDH systems, the N1s spectrum for Cu\textsubscript{2}Cr–NO\textsubscript{3} with a major component around 407.0 eV indicates the presence of NO\textsubscript{3}– counter ions in the inter-layer space of the LDH mineral network (additional peaks in the N1s spectrum at 399.3 eV and 403.6 eV correspond to the reduction of nitrates under the X-ray beam) (Table 2, see Fig. ESI2a in the ESI\textsuperscript{w}); in the case of Zn\textsubscript{2}Al–Cl, the Cl2p doublet (198.8 eV–200.5 eV) is in good agreement with Cl\textsuperscript{–} ions in the inter-layers space (see Fig. ESI2b in the ESI\textsuperscript{w}).

4.1.2 Guest organic molecules. In the following part, only results of the anionic headgroups (concerned in the interaction with the host matrix) are discussed (sulphur and oxygen for sulfonate function in HBS and carbon and oxygen for carboxylate function in HBC). The XPS examination of the HBS–Na\textsuperscript{+} salt done in ref. 16 puts into evidence the sulfonate environment at 167.9 eV–169.1 eV in the S2p peak (Fig. 5a) and confirmed the distinction between the –OH and –O\textsubscript{3}S
oxygen atoms in the O1s spectrum (Fig. 5b) in a 1/3 relative ratio (Table 2). For the HBC−,Na+ salt, the C1s peak allowed one to distinguish three types of environments: C–C/C–H (284.6 eV), C–OH (286.3 eV) and CO2 (288.2 eV), the component at 291.9 eV being associated with a π → π* satellite structure (Fig. 5c); relative percentages of the three components match with the chemical formula of the salt.

Caromatic/Cphenol (= 5.6) and C phenol/Ccarboxylate (= 1.1) relative proportions agree with the expected ratios of 5 and 1. The O1s spectrum (Fig. 5d) exhibits two components associated with the –OH and –O2C functions in 1 : 2 amount.

For HBS−,Na+ and HBC−,Na+ ions, a supplementary peak around 536.0 eV appears besides the O1s components which is assigned to the K1L1L23 Auger peak of sodium ions. Note that the –OH component is not located at the same position in the O1s spectrum of both salts. The 0.5 eV difference comes from a difference in the electronic structure/geometry relationship. The Na1s peak also shows a +0.4 eV binding energy difference which could traduce this global effect taking into account the chemical specificity of the two organic entities.

4.2 Intercalated systems

Once reference chemical environments are described, the analysis of hybrid systems was carried out with the main objective to probe the potential changes of the electronic structure of both the inorganic and organic systems when interacting together.

4.2.1 Zn2Al–HBS/Zn2Al–HBC hybrid materials: effect of the inserted organics. The morphology of the Zn2Al–HBS and Zn2Al–HBC hybrid materials has been studied by SEM (Fig. 1c,d). Zn2Al–HBC exhibits well defined and dispersed platelets with a size higher than 100 nm whereas those of Zn2Al–HBS are smaller and globally more agglomerated with each other. These observations would indicate that HBS−,Na+ intercalation tends to inhibit the crystallographic growth while HBC− insertion seems to favor it.

Experimentation performed with XRD has first confirmed the insertion process with the increase of the mineral matrix gallery height (+7.67 Å after HBS insertion and +7.32(5) Å after HBC insertion) (Table 1) in agreement with some
established interactions by H-bonds. Refinement convergences were satisfactory by using a hexagonal unit cell with the space group $R3$, resulting from a three layer polytype. Diffraction lines (006) and (003) are well-defined and symmetric for the hybrid materials (Fig. 2b and c) indicating the fine layered ordered stacking. Comparison of XRD patterns reveals the peculiarity of Zn$_2$Al–HBC for which lines are thinner and more intense. As previously considered on the basis of SEM results, the organic HBC$^-$ ion would play a major role in the crystallographic growth of the hybrid phase; this would be less pronounced for HBS$^-$ ions. Calculated crystallite size (Table 1) is around 130 nm in the case of Zn$_2$Al–HBS and 150 nm for Zn$_2$Al–HBC. After the organic insertion, the (00l) shift towards the small angle side attests to a real interlayer space enlargement associated with a slight deformation of the mineral sheets ($a$ parameter getting shorter). The contribution of the sulfonate group, heavier than the carboxylate, to the reflecting power of (0012) line can be noticed.

Previous results of the Zn$_2$Al–HBS hybrid material have also shown few changes in the XPS spectra of the sub-systems related to those of the separated precursors. Binding energies (Table 2) and experimental profiles of the mineral host elements kept unchanged with the intercalation of organic molecules (Fig. 3c,d). The peak full widths at half maximum (FWHM) were constant. The calculated atomic ratio Zn/Al is 1.64 for Zn$_2$Al–HBS and 1.61 for Zn$_2$Al–HBC. The low content of Zn$^{2+}$ ions is not usually observed when Zn$_2$Al–NO$_3$, Zn$_2$Al–CO$_3$ and Zn$_2$Al–Cl phases precipitate at pH = 8.5. The organic molecules should then have a direct impact in the final metal cation composition of the mineral layers. This phenomenon was already observed for the preparation of hybrid LDH/anionic porphyrin materials. Let’s note that an increase of the pH during coprecipitation of metal salts would raise the Zn/Al ratio up to the good stoichiometry but the undesirable phenol function dissociation of HBS and HBC enforces a fixed value of 8.5 for the pH.

When HBS molecules intercalate the host LDH material, the S2p peak profile changes even if no chemical shift is observed (BE$_{S2p} = 168.0$ eV–169.3 eV) (Fig. 6b). However a consequent widening of about 0.5 eV is noticed attesting to a new nearby atom population around the sulphur atoms (Table 2). Mineral layers globally remain stable (no change in FWHM of Al2p and Zn3p peaks) but recorded XPS data of sulfonates are more significant of the interactions with the adjacent hydroxyl functions. The interlayer organic entities mainly stabilize via H-bonds as reported in literature and observed elsewhere in the FTIR spectrum. Moreover, a characteristic C1s component at 289.1 eV is noticed as pollution traces of carbonates are found within the interlayer space. A vibration mode of carbonates at 1350 cm$^{-1}$ is also evidenced during FTIR analysis.

In the case of the Zn$_2$Al–HBC material, the mineral matrix is not concerned by some modifications attesting to the stability of the metal hydroxide network (Table 2). The C1s spectrum always shows the same three chemical environments as previously observed for HBC$^-$,Na$^+$ salt analysis. Close attention to the CO$_2$ component, at 288.6 eV, underlines the non-significant widening after intercalation from 1.1 eV to 1.2 eV. The XPS monitored very weak interactions between the mineral layers and the carboxylate groups which could assume the particular confinement of HBC molecules into the LDH. Relative amounts calculated from the XPS data for the
whole carbon components ($C_{\text{aromatic}}/C_{\text{phenol}} = 5.3$ and $C_{\text{phenol}}/C_{\text{carboxylate}} = 1.2$) are found in good agreement with the stoichiometry of the HBC molecule. The O1s spectrum of the two hybrid materials exhibits a sole peak at 531.8 eV ± 0.2 eV which is wider (FWHM is around 1.9 eV) than the initial O1s reference host matrix one (FWHM = 1.5 eV).

In the FTIR spectrum of Zn$_2$Al-HBC (Fig. 7), the intense band at 1748 cm$^{-1}$ corresponds to the stretching vibrations of the hydroxyl groups of both the layer hydroxide moieties and the interlayer water. The broadening of this band is generally due to hydrogen bond formation. The intense band at 1748 cm$^{-1}$ corresponds to the $\nu_{\text{COOH}}$ mode of the carboxylic species is not present anymore after HBC insertion. Bands around 499 cm$^{-1}$, 528 cm$^{-1}$, 568 cm$^{-1}$ and 607 cm$^{-1}$ are due to M-O lattice vibrations and attest to the quite ordered interlayer structure of the LDH upon intercalation. According to the comparison of data between the HBC salt and the Zn$_2$Al–HBC hybrid material in the 2000 cm$^{-1}$–1000 cm$^{-1}$ range, it is hard to observe a clear shift ($\sim 10$ cm$^{-1}$) for $\nu_{\text{c}}$ and $\nu_{\text{as}}$ modes of the CO$_2$ functions (even if these bands are less intense for the hybrid system) which would have clearly attested to the stabilizing H bonds of HBC molecules.

Concerning both HBS and HBC organic moieties, first theoretical calculations were achieved to understand differences noticed before with XPS (broader Zn3p, Al2p and S2p peaks for Zn$_2$Al–HBS). Actually, even if the $pK_a$ values of the organic compounds can roughly give a first overview of the possible reaction between basic mineral layers and acid molecules, the description of the sub-system connections might also be specified on the basis of the organic molecules' configuration or orientation. Modelling of the intercalation process confirmed the stabilization of the hybrid systems by hydrogen bonds (preferentially with the Al sites of the hydrotalcite) in agreement with the XPS data, with no great modification of the electronic environment around the carbon and sulphur atoms of the –CO$_2$ and –SO$_3$ groups (see Table ESI1 in the ESI†). For the HBS molecules, a ($q_c = +1.16$ e$^-$) net charge was found upon intercalation (for reference HBS salt, $q_c = +1.10$ e$^-$). The net charge calculated for the carbon atom of the carboxyl group in the Zn$_2$Al-HBC system ($q_c = +0.52$ e$^-$) is close to the reference anion value ($q_c = +0.49$ e$^-$). Those first theoretical data traduce a higher variation of charge for sulphur atoms in relation with the XPS S2p peak widening previously evoked.

The SO$_3$ trihedron geometry offers many possibilities of interactions (associated with different $\theta$ angles related to the mineral layer surface). The possible competition between several interactions leads to a higher disorder after the HBS intercalation compared to HBC. Actually, calculations of the rotation barrier gave values respectively equal to 0.16 eV (15.44 kJ mol$^{-1}$) for HBC$^-$ and 0.0018 eV (0.18 kJ mol$^{-1}$) for HBS$^-$. This result is consistent with the highest ease of rotation of the –SO$_3^-$ group towards the aromatic cycle compared with the –CO$_2^-$ group (for which the phenomenon of $\pi$ conjugation imposes a parallel conformation to layers). This could assume a more intense reactivity of the –SO$_3^-$ function towards the mineral layers when tumbling with then an enlarged XPS S2p peak upon intercalation. Whereas an oblique conformation is favoured for HBS molecules, HBC entities are energetically more stable when parallel to mineral layers. Net charges of Al$^{3+}$ centers (directly interacting with counter-ions) are almost unchanged upon intercalation as experimentally observed with constant Al2p XPS binding energy.

First XPS insights have shown the possibility to probe slight modifications of an atom’s chemical surroundings upon intercalation. The technique gives an original set of data to monitor electronic evolutions theoretically predicted; it appears like a suitable and complementary analysis tool to FTIR and PXRD.

### 4.2.2 Zn$_2$Al–HBS/Cu$_2$Cr–HBS hybrid materials: mineral matrix behavior upon intercalation

The next part of the study deals with the behavior of different LDH host systems as seldom reported in the literature. Examination of the HBS ions insertion process is then envisaged in a Cu$_2$Cr–NO$_3$ LDH host lattice in comparison with the previous Zn$_2$Al–Cl. The main purpose is to find if the copper–chromium matrix specificity affects the organic–inorganic interactions. The challenge was even to monitor these structural changes with the XPS.

On the SEM image (Fig. 1e), compared to the Cu$_2$Cr–NO$_3$ phase (Fig. 1b), crystallites of Cu$_2$Cr–HBS are smaller (Table 1) and the connection network between platelets appears more restricted. It would imply for Cu$_2$Cr–NO$_3$, the formation of a quasi-continuous network in a xerogel state. During the preparation, suspended particles would maintain connections after drying. The phenomenon could belong to the hygroscopic character of NO$_3^-$ ions which would participate in the H bonds network with the water molecules of the inter-layer space. The exchanged HBS$^-$ ion would adapt to the present mineral layers configuration by distorting the local arrangement of SO$_3$ functional group and by occupying more well-defined crystallographic sites than NO$_3^-$ positions.

For the hybrid Cu$_2$Cr–HBS phase, (00l) diffraction lines are symmetrical, thinner and well-defined giving evidence of a better crystalline degree than for Cu$_2$Cr–NO$_3$ (Fig. 2e). In comparison with the PXRD pattern of the reference Cu$_2$Cr–NO$_3$ phase (Fig. 2d) a clear enhancement of the
inter-layer space is noticed with the 5° shift to the small angles side of the (003) line. HBS molecules would favor a better crystalline degree of the hybrid material even if they seem to slow down the particles nucleation (bigger flakes with NO₃⁻ counter-ion, Table 1). The layers structure modified during the intercalation process with a +0.03 Å increase of a parameter (Table 1). This trend differs from Zn₂Al–HBS (Δa = −0.007 Å) certainly due to the deep ability of Cu²⁺–O₆ octahedrons to distort. While the Zn₂Al-network offers a real stability towards the organic molecules which easily adapt their conformation within the inter-layers space, the Cu₂Cr-matrix seems to make easier the intercalation process and stabilize the whole hybrid structure by expanding whatever the direction. At this point of the study and in order to propose an organic molecules arrangement between the LDH layers, the inter-layer space available for HBS⁻ anions was compared with the anion size (8.64 Å) calculated by a theoretical approach (Gaussian code[50]). Considering the non-planar Cu₂Cr layers surface, the gallery height, calculated from the PXRD data, represents a mean available space for the HBS⁻ ions. Values found for both hybrid materials basically show different behavior; in the assumption of a monolayer insertion, the inter-layer spaces are too small to envisage a perpendicular arrangement of the HBS⁻ anions. Then, considering the molecules tilt, the minimum θ angles calculated related to the normal direction of the LDH stacking are specific for both hybrid materials: 23.69° for Zn₂Al–HBS and 25.27° for Cu₂Cr–HBS.

For the prepared Cu₂Cr–HBS material aged at room temperature for 72 h, the XPS analysis only show a small widening for copper (+0.3 eV) and chromium peaks (+0.2 eV) (Table 2, Fig. 4c and d) as HBS molecules exchanged with NO₃⁻ ions. The z’ Auger parameter measured at 1851.0 eV confirms the relative electronic stability of the mineral layers even if the decrease of Cu2p I_sat/I_main ratio to 0.68 indicates the beginning of a structural evolution.

No XPS S2p peak shift is noticed but a strong widening of the peak from 0.9 eV to 1.5 eV is recorded (Fig. 6d) as already noticed for Zn₂Al–HBS. Modification of the local environment around SO₃ functions is influenced by the nature of the host LDH system; Cu₂Cr LDH structural specificities should have a greater incidence on the strength of sub-system interactions. The XPS examination of oxygen 1s core level is not discussed because of the complex interpretation due to the overlapping of the HBS phenol group signal with the oxygen atoms of the main headgroup (sulfonate) and the hydroxide bonds of the mineral layers. The O1s peak observation, for the hybrid Zn₂Al–HBS material, shows a +0.4 eV broadening which traduces a real change in the oxygen surrounding. Small change is noticed (+0.1 eV) for Cu₂Cr–HBS. In the Cl2p and N1s regions a void signal has been recorded attesting to the effective HBS⁻ ↔ Cl⁻/NO₃⁻ anion exchange (see Fig. ESI2b in the ESI†).

Considering the host matrix nature, the insertion process is differently transcribed through the XPS results. Small evolutions had been mentioned for the Zn₂Al–HBS and Zn₂Al–HBC systems compared to the associated LDH precursors but had suggested some possible interactions in quite long distances via H-bonds (only peak broadenings are observed but no chemical shifts are detected). Results obtained for Cu₂Cr–HBS are quite similar and would indicate the existence of identical sub-system interactions.

4.3 Thermal treatments and grafting process

Additional experiments were also performed by heating up the different hybrid samples to make denser the inorganic/organic interactions and to consequently interpret the XPS signal.

In situ PXRD patterns reported in Fig. 8a, clearly evidence a two step process of structural contraction for the Zn₂Al–HBS material: a distinct contraction around 80 °C (00l lines shift to the low angle side), quickly followed at 100 °C by a slight extension (00l lines turn back to the high angle side) of the inter-layer space. This evolution traduces a critical contraction/extension area associated with a structural re-arrangement of the organic anions within the host LDH matrix. Between 100 °C and 200 °C, the hybrid phase presents an inter-layer distance (Table 1) of about 13.40 Å lower than the room temperature value (15.39 Å). The LDH structure is then preserved and the very low a parameter variation (Δa = −0.008 Å) attests of the stabilizing influence of the anions via their specific anchorage modes to the mineral sheets. Particle size drastically decreases upon thermal treatment (100 nm at 200 °C, 130 nm at RT). Beyond 200 °C, the inter-layer distance goes down to 11.25 Å and the LDH network starts strongly collapsing from 300 °C with the sole distinguishable (003) line on the PXRD pattern. The partial lamellar character is preserved until the whole organic molecules combustion (around 500 °C) as already observed by S. Bonnet et al. in the case of a Zn₂Al-phase intercalated with functionalized porphyrins.[47] Analysis of Cu₂Cr PXRD pattern (Fig. 8b) shows the hybrid LDH structure is clearly evidenced till 200 °C mainly confirmed with the presence of (012) and (110) lines. By increasing more the temperature, these lines disappear revealing some bonds breaking down in the mineral sheets and some mixed oxide phases are observed. Crystallites are half as big at 200 °C compared to RT (Table 1). When the Zn₂Al–HBS PXRD study mostly highlighted a two step contraction phenomenon, only a simple contraction is noticed for Cu₂Cr–HBS with the organic molecules condensation onto the LDH layer occurring early at 40 °C. Precautions taken in the synthesis of this material (aging at room temperature) were then necessary to ascertain the study of an only intercalated state in section 4.2. Effectively, hybrid material aged at 70 °C was grafted at this temperature. The inter-layer distance goes down to 13.20 Å which is relatively low (2.00 Å contraction of the inter-layer space) for a LDH hybrid phase intercalated with a bulky anion like HBS⁻ (Table 1). Beyond 200 °C, the signal of the LDH network starts disappearing as multiple broken bonds in the Cu₂Cr(OH)₆⁺ layers are produced and some metal oxides and mixed metal oxides domains grow up at the same time. Actually, some new reflection lines rise up which could be associated with Cu₂SO₄ (JCPDS file no. 01-1081), CuO (JCPDS file no. 80-1917), Cu₂Cr₂O₆ (JCPDS file no. 34-0424), Cr₂O₃ (JCPDS file no. 84-1616) and Cr₂(SO₄)₃ (JCPDS file no. 81-1834: 15.79° (Cu₂SO₄ (220)), 20.80° (Cr₂(SO₄)₃ (104)), 24.87° (Cr₂(SO₄)₃ (113), Cr₂O₃ (012)), 20.80° (Cr₂(SO₄)₃ (104)), 24.87° (Cr₂(SO₄)₃ (113), Cr₂O₃ (012)),
29.62° (CuCr₂O₄ (200)), 35.57° (CuO (002), CuCr₂O₄ (211)), 36.03° (Cr₂O₃ (110)), 38.69° (CuCr₂O₄ (202), Cr₂(SO₄)₃ (104), CuO (111), (200)) and 42.40° (CuCr₂O₄ (220)). Some XPS surveys were carried out at temperatures for which the organics are grafted onto the mineral matrix; these temperatures being low enough to prevent any exfoliation of the host LDH structure. XPS analysis temperatures were chosen on the basis of in situ PXRD measurements done gradually at different stages from 25 °C to 300 °C to precisely follow the structural high sensitivity of the hybrid system.

The Zn₂Al–HBS phase was then thermally treated at 200 °C in an oven before XPS monitoring, this adapted temperature ensuring the organics anchorage in a preserved well-defined LDH network. Results for the heated hybrid system show a significant shift of the S2p peak with the thermal treatment (+0.6 eV) (Fig. 6c, Table 2) which tends to express the higher positive character of sulphur atoms in agreement with a new electronic distribution along the S–O bonds. The estimation of the ΔBE (O1s–S2p), which generally gives a good overview of such change in the S–O bonds, has shown a decrease of this binding energy difference (363.3 eV at 200 °C, instead of 363.8 eV for Zn₂Al–HBSRT). This value is significant of a higher ionic character of the S–O bond than for HBS salt. The theoretical calculations run from a grafted system geometry (see table ESI1 in the ESI) had highlighted the increase (+0.13e⁻) of the sulphur atoms net charge.

Fig. 8 In situ PXRD patterns of (a) Zn₂Al–HBS and (b) Cu₂Cr–HBS with basal spacing evolution.

* : oxide phases

LDH network. Results for the heated hybrid system show a significant shift of the S2p peak with the thermal treatment (+0.6 eV) (Fig. 6c, Table 2) which tends to express the higher positive character of sulphur atoms in agreement with a new electronic distribution along the S–O bonds. The estimation of the ΔBE (O1s–S2p), which generally gives a good overview of such change in the S–O bonds, has shown a decrease of this binding energy difference (363.3 eV at 200 °C, instead of 363.8 eV for Zn₂Al–HBSRT). This value is significant of a higher ionic character of the S–O bond than for HBS salt. The theoretical calculations run from a grafted system geometry (see table ESI1 in the ESI) had highlighted the increase (+0.13e⁻) of the sulphur atoms net charge.
This evolution confirms the XPS S2p variation upon thermal treatment at 200 °C. The Al2p experimental profile widens while Zn3p peak keeps unchanged (Fig. 3e and f). Consideration of zinc surrounding inertia was the starting point for modeling the hybrid material in a pillared configuration (organic entities are supposed to graft onto the LDH layers via aluminum centers). The theoretical study had concluded to a double bridging attachment of the HBS molecules onto the mineral sheets ensuring the relative good stability of the whole hybrid material.16 New theoretical calculations were enganged considering different possibilities of grafting: with a single or double attachment of HBS molecules (calculations do not converge for a three bonds attachment of the SO3 trihedron). These first tests led to a real change of \( q_{\text{AI}} \) in relation with the XPS Al2p broadening. The single anchorage visualization appears more adapted to describe the grafting phenomenon as \( q_{\text{AI}} \) in the case when a double bond strongly decreases. Such important variation should be transcribed with a clear chemical shift of the XPS Al2p peak. All this information confirms the reliability of the XPS technique to probe connections set up between systems. Finally the estimation of the overlapped population along the \( S\text{-}O \) bonds reinforces the loss of covalent character previously deduced from \( \Delta \text{BE(O1s–S2p)} \). Calculations clearly show an important decrease (−0.131 e\text{\textperiodcentered}) and the trend is observed in the case of Al–O bonds (−0.116 e\text{\textperiodcentered}).

For the copper/chromium hydroxide matrix, a multi-temperature XPS survey was engaged to progressively follow the grafting phenomenon and the LDH network changes via the Auger parameter. As discussed in the first part of the paper, in the case of the copper element, beside the core levels analysis, the estimation of the Auger parameter (\( z' \)) is a fine probe to investigate sensitive structural and electronic changes. The apparent Auger parameter calculated goes up to 1851.4(5) eV (instead of 1851.0 eV for the hybrid material at room temperature) when increasing the temperature up to 40 °C. That was the reason Cu2Cr–HBS hybrid material was not ageing in an oven in mild temperature conditions after its preparation. The \( I_{\text{sat}}/I_{\text{main}} \) ratio increases to 0.73 which is higher than for room temperature (0.68). This value undeniably attests to a copper coordination modification as reported for copper-based spinel materials.40 As previously mentioned, the Cu2p\( 3/2 \) line is located at 934.5 eV for the hybrid material at room temperature, but shifts to 935.2 eV early at 40 °C (Fig. 4e). On the basis of the new S2p peak (BE: 168.3 eV–169.6 eV) (Fig. 6e), the calculated \( \Delta \text{BE(O1s–S2p)} \) around 363.2 eV at 40 °C would attest to \( S\text{-}O \) bonds being more ionic under grafting. The Cu2p\( 3/2 \) binding energy stays unchanged till 250 °C when the LDH stacking starts collapsing. Beyond 250 °C, the Cu2p\( 3/2 \) peak slowly shifts to the low binding energy side (≈ 934.0 eV) and enlarges (+0.5 eV), traducing the system evolution towards a complex equilibrium between partial lamellar hybrid material and mixed oxides phases. Between 40 °C and 200 °C, even if copper 2p binding energies do not change (Fig. 4e/4g, Table 2), the \( z' \) value slightly increases up to 1851.6 eV (200 °C) traducing the progressive evolution of the chemical surrounding and providing a new screenshot of the structural changes. A chemical shift of about +0.8 eV with an important enhancement of the FWHM (+0.4 eV) is noticed for the Cr2p\( 3/2 \) peak after heating up the hybrid phase to 40 °C (Fig. 4f, Table 2). The constant 577.7 eV binding energy recorded for the Cr2p\( 3/2 \) line in the 40 °C–200 °C (Fig. 4f, h) range is quite similar to data reported in the work of M.C. Biesinger et al.48 for a Cr(OH)3 compound heated at 50 °C. No evidence of multiplet components is seen. Globally, both copper and chromium metal centers of the LDH hydroxide layers get more positive with the thermal treatment and would suppose some electronic transfers from the metal atoms towards special other centers. Changes observed in the O1s spectrum with a 0.4 eV chemical shift to the low energy side could assume some metal → oxygen electrons transfers. Beyond 250 °C, the chromium surrounding is still evolving as the Cr2p\( 3/2 \) component keeps on shifting (+0.2 eV) and widening (+0.6 eV). Moreover, sulphur atoms are found in a well-identified SO4 environment (S2p BE: 169.0 eV–170.2 eV49), probably interacting with the modified host material. As reported in a recent paper of W. Zhang et al.,50 a possible representation of the copper hydroxide environment in relation with the proximity of sulfate entities can be given. Hydroxide corrugated layers are formed by edge sharing of distorted Cu(OH)\(_6\) octahedra because of the Jahn–Teller effect. Such deformed octahedra stem from a structural pattern in which the four shortest bonds of Cu–OH around a Cu(\( \text{II} \)) ion yield a roughly planar Cu(OH)\(_6\) unit. The latter OH groups would be involved in the interaction with the organic molecules. By increasing the temperature up to 300 °C, PXRD measurements reveal the full exfoliation of the LDH structure to some well-defined (on the basis of reference compounds PXRD and XPS analysis) but un-organized mixed oxides domains. XPS results allow one to identify some of these phases like the CuO with Cu2p lines at 933.9 eV and the Cr2O3 and Cr2(SO4)3 with the Cr2p lines at 576.3 eV and 578.5 eV (see Fig. ESI4 in the ESI).51–54 Moreover, the \( I_{\text{sat}}/I_{\text{main}} \) ratio of the hybrid material at 300 °C is the same as the manufactured (Aldrich) 2CuO,Cr2O3 one (0.81(5) for Cu2Cr–HBS 300 °C and 0.83 for the mixed metal oxides reference system) which confirms the reliability of the XPS in the monitoring of chemical environments changes (see Table ESI2 in the ESI).

5 Conclusion

In summary, the present investigation has led to new information about the inorganic–organic interactions within LDH hybrid material derivatives. 4-Phenol sulfonate (HBS) and 4-phenol carboxylate (HBC) species intercalated with LDHs were studied. PXRD results have evidenced a pronounced enhancement of the Zn\(_2\)Al LDH basal spacing (+7.67 Å with HBS and +7.32 Å with HBC). The original XPS survey put into evidence small changes in the full width at half maximum of zinc and aluminum core levels revealing few disturbances in their local chemical surrounding. On the contrary, HBS organic molecules seem to feel a larger effect of intercalation in the LDH network as the associated XPS signal clearly evolves with a general widening of sulphur peaks (in relation with the well-known hydrogen bond-like interactions between both sub-systems). In the case of Zn\(_2\)Al–HBC, organic entities
do not electronically change which was interpreted as a parallel insertion between the LDH layers.

In the second part, a thermal treatment was carried out to make the interactions denser. A simultaneous study was made on Zn\(_2\)Al–HBS and Cu\(_2\)Cr–HBS hybrid materials in order to determine the potential behavior of the host material with the temperature. The grafting of 4-phenol sulfonate ions would occur by single bonding to the inorganic layers, where only a contraction event was noticed for Cu\(_2\)Cr–HBS. From then on, the temperature was 40 °C. XPS experiments monitored the drastic electronic evolution of the sulfonate function as the S2p peak clearly shifted from around 0.5 eV. Only strong anchorage to the inorganic LDH layers could explain such a binding energy change. First theoretical modeling has shown charge transfers between atoms involved in the organic condensation and a decrease (loss of covalent bonding) has shown charge transfers between atoms involved in the organic condensation and a decrease (loss of covalent bonding). The grafted 4-phenol sulfonate ions would occur by single bonding to the inorganic layers, where only a contraction event was noticed for Cu\(_2\)Cr–HBS.

References