Quantification by Powder X-ray Diffraction of Metal Oxides Segregation During Formation of Layered Double Hydroxides

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Abstract — A simple, easily applicable method is proposed to quantify the amount of ZnO segregated during synthesis and post-synthesis treatments of Zn-Al layered double hydroxides with the hydrotalcite structure. The method provides a feasible, easy, fast, and reliable way to get values for ZnO content, and the method can be extended to other compounds.

Index Terms — Hydrotalcite, LDH, PXRD, ZnO.

I. INTRODUCTION

Layered Double Hydroxides (LDHs) have proven to be solids with chemical versatility and exceptional properties that make of them solids with different applications in Industry and Medicine, among many other fields [1]-[9]. The structure of LDHs can be explained on the basis of the brucite, Mg(OH)₂, structure, formed by a hexagonal close packing of hydroxyl anions, where all octahedral holes every two interlayers are occupied by Mg²⁺ cations. The partial isomorphic substitution of divalent cations by trivalent ones leads to a net positive charge, which is balanced by insertion of anions (together with water molecules) in the originally empty interlayers. For this reason, LDHs are also sometimes known as anionic clays, due to similarities and differences with well-known clays. Many different divalent and trivalent metal ions can be incorporated into the brucite-like layers, with the unique requirement that the cations should have the adequate size to occupy the octahedral sites. Furthermore, both organic and inorganic anions of different sizes and charges could be incorporated in the interlamellar space [10]-[12].

There are many divalent and trivalent metal cations which fulfill the conditions to form LDHs, but, in some cases, segregation of hydroxides or oxides of one of them is observed. The determination of the amount of segregated metal cation in the final solid, and therefore outside the lamellar structure, has a great importance both for the structural determination of the solid as well as for its future application on fields such as catalysis or adsorption processes. Usually, the chemical formula of hydrotalcite-like compounds is determined by element chemical analysis (generally restricted to the metal cations in the brucite-like layers), usually combined with thermal decomposition studies (which lead to formation of the metal oxides) to determine the amount of water, and FT-IR spectroscopy (to identify the interlayer anion), without considering other aspects. So that, if in addition to the solid with the LDH structure, a portion of the cations determined by element chemical analysis is forming an oxide, the composition and chemical formula calculated for the LDH does not conform to the real one. This fact has a great importance on the determination of the structural and textural properties of the solids. In the precursor method, widely applied to prepare heterogeneous catalysts, the active mixed oxides are obtained sometimes by calcination of hydrotalcite-like compounds, thus forming mixed oxides with a high homogeneity degree as a consequence of the homogeneous distribution of the cations in the brucite-like layers. Thus, when obtaining catalysts from precursors with really consist of a mixture of an oxide and the LDH, where some of the cations may even be in different coordination environments, the homogeneity in the dispersion of the metal cations in the final mixed oxide could be negatively affected, impacting on the dispersion of the active phase and on the acid-base and catalytic properties of the oxide surface. The possibility of segregate oxide phases has special relevance when using the dissolution-precipitation method when these materials are submitted to pillaring processes to obtain compounds with the LDH structure of great interest. Kooli et al. have reported that for large Ni/Al or Mg/Al ratios, dissolution of magnesium or nickel cation occurs during pillaring with polyoxometalate anions, precipitating the most stable specie of divalent and/or trivalent polyoxometalate salts [13].

In other cases, segregation is favored by the limited stability of the metal cation in the octahedral geometry provided by the brucite-like layers, especially if the raw samples are submitted to post-synthesis treatments to improve their properties (e.g., crystallite size, porosity, specific surface area, etc.). In these cases, the cation is partially segregated to form more stable species, which crystallize together with the LDH. Although qualitative
identification of this segregated species can be straightforward done from X-ray diffraction analysis, its quantification can be somewhat difficult [14].

Cations such as Mg$^{2+}$ form almost exclusively compounds where the cations are in an octahedral environment, but other cations able also to form LDHs, such as Zn$^{2+}$ or Co$^{3+}$, form stable compounds where the cations are in both octahedral or tetrahedral environments [15]-[17], and so such a segregation can be hardly avoided. This situation clearly exists in the case of Zn-Al LDHs which, upon submission to hydrothermal treatment (well under standard conditions or with microwave irradiation), segregate ZnO, where Zn$^{2+}$ cations are in a tetrahedral environment [18], [19].

For all of these reasons, it seems convenient to have a fast and reliable method that allows quantification of the amount of segregated oxide from hydrotalcite-like compounds in its synthesis stage.

In this communication, we report a simple procedure to identify and to quantify the presence and amount of Zn$^{2+}$ oxide formed when Zn-Al LDHs are submitted to different post-synthesis treatments, which are usually applied to improve their properties.

II. EXPERIMENTAL

A. Synthesis of the samples

The LDH solids were prepared by the coprecipitation method [20]. The syntheses were carried out in previously boiled, decarbonated water solution, and nitrogen was continuously bubbled through the solution to avoid contamination from atmospheric CO$_2$ and intercalation of carbonate ions in the interlayer of the solids instead of pursued nitrate. Reagents Zn(NO$_3$)$_2$:6H$_2$O (98-102%), Al(NO$_3$)$_3$:9H$_2$O (98-102%), NaOH (98%) and ZnO (99%) were purchased from Panreac and used as received, without any further purification. An aqueous solution of the nitrate salts of the metal cations was prepared by dissolving 50 mmol of Zn(NO$_3$)$_2$:6H$_2$O and 25 mmol of Al(NO$_3$)$_3$:9H$_2$O in 300 mL of decarbonated water.

The metal cations solution was dropwise added over a basic (NaOH 1M) solution, which pH was fixed to 10 by adding HNO$_3$. Once the precipitation began, the solution was kept under vigorous magnetic stirring and the pH of the reaction mixture was kept at a preselected value (pH=10) by adding the required amount of 2 M NaOH from a 240 CRISON pH-burette. When the addition was complete, the suspension was further stirred for 1 h at room temperature. The precipitates were separated and washed by centrifugation with distilled water until a pH close to 7 was reached, in order to remove the balancing ions from the starting salts. Finally, the solids were dried at 40 °C in an oven in open air.

B. Characterization techniques

The powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D-5000 instrument using Cu-Kα radiation (λ = 1.54050 Å) and a scanning rate of 2 °/min with fixed divergence, from 5° to 70° (2θ).

The FT-IR spectra were recorded in a Perkin-Elmer Spectrum One instrument with a nominal resolution of 2 cm$^{-1}$ from 4000 cm$^{-1}$ to 450 cm$^{-1}$, using KBr pressed pellets and averaging 100 scans to improve the signal-to-noise ratio.

Elemental chemical analyses for Zn and Al were carried out by ICP-OES in a Yobin Ivon Ultima II apparatus, in NUCLEUS (University of Salamanca, Spain).

III. RESULTS AND DISCUSSION

During the synthesis of Zn-Al LDHs, formation of a single, pure phase is difficult because of the simultaneous formation of a ZnO phase. In order to identify the amount of ZnO in the sample, we have developed the method here described. This methodology is based on the ratio between the areas of the most characteristic XRD reflections of each phase, and its relationship with the quantities of substance present in the mixture.

This approximation has been used by Inayat et al. for the quantification of the relative amount of nitrate in parallel or tilted orientation in the interlayer of Zn-Al nitrate LDHs [21]. The method is a fast and simple approximation as assessment in the synthesis of the materials in the laboratory and in any case can substitute more precise methods.

To develop this method, a series of samples were prepared by mechanical mixing of Zn-Al LDH, prepared as detailed above, with pure commercial ZnO (Zincite phase, ICDD 36-1471). Knowing the mass percentage in which they are mixed it is possible to relate the ratio of the areas of the most characteristic XRD reflections of each phase with the mass percentage in the mixture. This relationship will hopefully allow to determine the equation of the calibration line, which will then be used for estimating the mass ratio of each phase in new synthesized samples.

The structures of the compounds were determined by PXRD. In the case of Zn-Al-nitrate the diffractogram shows the usual pattern observed in hydrotalcite-like compounds and is in agreement to the reported by Conterosito et al. [22]. In the case of ZnO the diffractogram matches the ICDD file 36-1471, corresponding to the Zincite phase.

The most intense reflections are indexed as (003) at 8.93 Å for the LDH compound and (101) at 2.48 Å for ZnO (Fig.1). These reflections are the best choice for our purpose. However, the (101) reflection for ZnO lies in a region, around 35° in 2θ scale, where other reflections of the Zn-Al compound may interfere in the quantification. In order to confirm the non-overlapping of the (101) reflection of ZnO with the LDH reflections, the cell parameters were calculated for a hexagonal symmetry in a 3R polytype from the spacings of the (003) and (110) reflections of Zn-Al LDH (Fig.1) at 9.95° 2θ and 60.45° 2θ, respectively, according to the procedure described elsewhere [4]. Based on these cell parameters, 3.06 Å for a and 26.67 Å for c, the positions of the most relevant LDH reflections were calculated using the equation in Gay [23] for a hexagonal lattice, obtaining the values listed in Table 1. The calculated (003) and (110) reflections in table 1 are practically identical from those read on the diffractogram to calculate the cell parameters. Finally, we can observe that the (101) reflection for ZnO lies just between (012) and (015) reflections for the LDH. The lack of overlapping is confirmed by the Full Width at Half Maximum (FWHM) values for (101) reflection included in Table 2.
which varies between 0.18 and 0.19 Å. In any case, the intensities observed and calculated for the (012) and (015) reflections in the LDH are very low, around 2%. So, no extra calculus as deconvolution or more complex techniques are needed.

The most intense reflection ascribed to the diffraction by planes (003) was recorded close to 10.0° (2θ) with a spacing of 8.93 Å. This interlayer space value is in agreement with a LDH phase with nitrate as the interlamellar anion and a MII/MIHI molar ratio close to 2 [11]. The diffraction by planes (006) was recorded close to 20.0° (2θ) with a spacing of 4.46 Å. The PXRD pattern of the Zn-Al LDH shows also a weak reflection at 11.5° (2θ) with a d-value of 7.69 Å, overlapped with the sharp, intense, reflection at 10° (2θ). Such a double reflection has been sometimes reported [24] to be due to the presence of nitrate anions in the interlayer with two orientations, namely, parallel and perpendicular (or tilted) to the brucite-like layers; as the nitrate anion does not show a spherical, but planar, shape, its size in two directions (perpendicular or parallel to the molecular plane) will be different. In order to explain the origin of this reflection, the solid was studied by FT-IR spectroscopy to identify the possible interlamellar anionic species. The FT-IR spectrum of pure Zn-Al LDH sample is shown in Fig. 2. The spectrum shows the characteristic broad band at 3460 cm⁻¹ due to the stretching vibration of hydroxide groups in the layers of LDH and of interlamellar water molecules. The band at 1624 cm⁻¹ is due to the bending vibration mode of the interlayer water molecules. The band at 1385 cm⁻¹ confirmed the presence of nitrate anion in the interlayer space, as this band is attributed to its ν₁(E') stretching vibration mode [25]. The very weak peak at 1050 cm⁻¹ is due to mode ν₁ of nitrate, which is forbidden in a D₃h symmetry; its presence in the spectrum means that the symmetry of the nitrate anion is somewhat distorted in the interlayer or that interlayer nitrate species exist in two different geometry environments, as suggested by the PXRD data reported above. It is also possible to observe the band at 826 cm⁻¹ corresponding to mode ν₂(A₂ₑ) of NO₃⁻ and the narrow band at 1763 cm⁻¹, a combination band of the nitrate vibration modes ν₂(A₁₆) at 1068 cm⁻¹ and ν₄(E') at 692 cm⁻¹. A band recorded at 615 cm⁻¹ corresponds to the M-OH vibration modes.

From the FT-IR analysis, it could be confirmed that nitrate is the only anion in the interlayer region. If nitrate is located parallel to the brucite-like layers, it would retain its D₃h geometry (as in the isolated molecular ion), and under this symmetry, mode ν₁ is forbidden in IR spectroscopy. However, if some of the nitrate anions are tilted with respect to the brucite-like layers, then the three oxide anions are no longer equivalent (because of their interaction with the layers) and thus the symmetry is decreased, probably to C₂ᵥ; under these circumstances, mode ν₁ becomes allowed, and would be responsible for the weak absorption band recorded at 1050 cm⁻¹. These results confirm that the double reflection recorded close to 10° (2θ) is due to the presence of nitrate anions in two different geometries in the interlayer.

The element chemical analysis provided a Zn and Al mass percentage contents of 32.64 % and 6.29 %, respectively, and as the FT-IR study confirmed the exclusive presence of nitrate in the interlayer, with no traces of carbonate from atmospheric CO2, the following formula could be calculated for this compound: [Zn₆₆Al₃₋₃(OH)₃] (NO₃)₅₋₅ · nH₂O.

This pure LDH phase was used to prepare samples with different known amounts of ZnO. Samples prepared contained 1, 2, 3 and 5 % mass of ZnO. Larger contents of ZnO were not studied as, if the aim of the work is to synthetize a pure LDH, impurities content larger than 5% would not be acceptable. All samples where characterized by PXRD, and their diffraction diagrams are shown in Fig. 1, where it is possible to distinguish both crystalline phases.

The more characteristic reflections of each phase selected for this analysis were the (003) basal reflection of the LDH and the (101) basal reflection of ZnO. Their reflection areas were calculated by using commercial software and are collected in Table 2. The ratio values between both areas (also included in Table 2) are plotted vs. the ZnO mass percentage in Fig. 3; obviously, a linear relationship between both magnitudes holds.

![Fig. 1. PXRD curves of prepared samples.](Image 49x559 to 288x730)

![Fig. 2. FT-IR spectrum of Zn-Al LDH.](Image 2192)

**TABLE I: CALCULATED POSITIONS OF THE LDH REFLECTIONS**

| h | k | l | d (Å) | 2θ (º) |
|---|---|---|-------|--------|
| 0 | 0 | 3 | 8.89 | 9.94 |
| 0 | 0 | 6 | 4.45 | 19.95 |
| 0 | 1 | 2 | 2.60 | 34.46 |
| 0 | 0 | 9 | 2.96 | 30.12 |
| 0 | 1 | 5 | 2.37 | 37.86 |
| 1 | 0 | 8 | 2.07 | 43.58 |
| 1 | 1 | 0 | 1.53 | 60.43 |
| 1 | 1 | 3 | 1.51 | 61.42 |

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A regression analysis was carried out by the least squares method, setting the corresponding equation. In order to have the best predictive model and not use a high grade polynomial, the lineal regression analysis was carried out (Fig. 3). The equation calculated was:

$$y = 0.0118x + 0.0008$$  \hspace{1cm} (1)

with a regression coefficient of 0.9997, and where y stands for the area ratio of the (ZnO/LDH) reflections and x for the ZnO mass content (percentage).

We then have checked how the equation (1) can determine the ZnO content in mixtures where the content is known beforehand, e.g., the ZnO content values for the reference samples. The results are included in Table 3. As it can be seen, the values calculated fit remarkably well with the real ones.

### Table III: Nominal and Calculated ZnO content in Reference Samples

| Sample  | Calculated ZnO content (%) | Relative error (%) |
|---------|-----------------------------|---------------------|
| 5% ZnO  | 4.99                        | 0.2                 |
| 3% ZnO  | 2.98                        | 0.7                 |
| 2% ZnO  | 2.04                        | 2.0                 |
| 1% ZnO  | 1.03                        | 3.2                 |

The predictive ability of this method was tested for different samples (S1-S4) prepared in our laboratory [19] following the same method described above, but adding methyl, dimethyl, or trimethyl amine to the reaction medium, and then they were submitted to hydrothermal treatment. The data calculated from their corresponding PXRD diagrams are given in Table 4, where the results of the analysis are also included.

Finally, it should be stressed that only minor, non-significant differences were observed when different commercial ZnO samples with different grain size or after hand milling were used for this analysis.

### Table IV: ZnO Mass Calculated for Prepared Samples

| Sample  | (101) reflection area (ZnO) | (003) reflection area (LDH) | Area ratio (101)/(003) | ZnO content (%) |
|---------|-----------------------------|-----------------------------|------------------------|-----------------|
| S1      | 121                         | 234                         | 0.51                   | 1.01            |
| S2      | 419                         | 9086                        | 0.0461                 | 2.01            |
| S3      | 72                          | 35695                       | 0.0020                 | 0.07            |
| S4      | 1141                        | 11106                       | 0.1027                 | 5.42            |

### IV. Conclusions

A method for quantitative determination of crystalline impurities formed during synthesis or upon post-synthesis treatment of LDHs has been developed. The method can be safely applied to any sort of compounds, if care is taken to record the diffraction diagrams for the control samples (to build the correlation curve), using the same experimental conditions as for the mixture to be analyzed. The method is accurate enough and avoids the use of more time consuming or complicated procedures.

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