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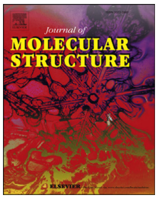

Dependence of bonding interactions in Layered Double Hydroxides on metal cation chemistry

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ABSTRACT

The evolution of various Infrared bands of Layered Double Hydroxides (LDH) with variable Zn:Al ratio was analyzed to correlate it with the changes in octahedral metal cation chemistry, interlayer carbonate anion and hydroxyl content of LDH. The synthesized phase-pure LDHs were crystallized as hexagonal 2H polytype with a Manasseite structure. The broad and asymmetric hydroxyl stretching region (2400–4000 cm^{-1}) can be deconvoluted into four different bands. With increase in Zn^{2+}:Al^{3+} metal ratio, the peak position of stretching frequencies of Al^{3+}–OH and carbonate-bridged hydroxyl (water) decrease almost linearly. Individual band's peak position and area under the curve have been successfully correlated with the carbonate and hydroxyl content of LDH. Due to lowering of symmetry of the carbonate anion, the IR-inactive peak $\nu_{C-O,\ symm}$ at 1064 cm^{-1} becomes IR active. The peak position of metal-oxygen bands and carbonate bending modes are practically unaffected by the Zn^{2+}:Al^{3+} ratio but the area under the individual M-O bands shows a direct correlation.

1. Introduction

Layered Double Hydroxides (LDHs) belong to the family of layered anionic clays which find diverse interesting applications such as catalyst [1–3], adsorbent material [4], supporting matrix for sensors [5–7], filler in organic dyes to enhance photo physical properties [8–10], fire resistant coating [11] and to modify the mechanical properties of polymer nanocomposite [12–14] etc. These spectacular properties are achievable because pure LDH can be easily synthesized with control over its tunable metal cation chemistry, interlayer anion and texture. Further, it can be functionalized by intercalation, grafting and controlled calcinations to generate required numerous functionalities. The chemical formula of LDH is represented as $[M^{II}_{1-x} M^{III}_{x} (OH)_2]^{Z+} A^{n-}_{Z/n}. y H_2O$ (M^{II}, M^{III} represents bi and tri valent metal ion, A^{n-} is the exchangeable interlayer anion and 'x' is layer charge). The first half represents the 2-D layer composition and the second half interlayer composition. The structure is based on that of brucite type layer where some of the bivalent metal ions are replaced by the trivalent metal ions and the anions are intercalated in interlayer position to maintain the electro neutrality. Schematic of LDHs showing edge sharing octahedrons of bi and tri valent metal ions along with the interlayer water and carbonate anion are shown in Fig. 1. The chemistry of octahedral layer (i.e. metal cations and its stoichiometry) can be easily varied to generate LDH of different layer charge. Apart from possessing different ability for intercalation, these LDHs can be calcined to generate an interesting "mixed metal oxide" (MMO) where the octahedral cations are statistically mixed in atomic level, giving rise to unique catalytic activity. Several recent reports discuss the promising application of such MMOs [1,15–17].

XRD and vibrational spectroscopy are two major tools to investigate the bonding interaction in LDH. XRD is an accurate method to reveal the crystallography, lattice strain, crystallite size and detailed atom positions in unit cell. However, due to lower crystallinity (and subsequently low scattering intensity) of most sub-micron sized LDHs and the presence of its various polytypes, analysis of XRD data (e.g. Rietveldt refinement) becomes difficult and inaccurate. Also, XRD cannot provide much information about structural changes after grafting reaction and calcinations (e.g. MMOs) – both of which have important consequences on its application as catalyst and functional material. In this backdrop, IR spectroscopy can provide very useful structural information which can be correlated to its properties. The origin of the infrared spectra is a mechanical vibration of the molecules, which are governed by the molecular symmetry of that molecule and the set of vibrations can be correlated with the specific orientation of the molecules in

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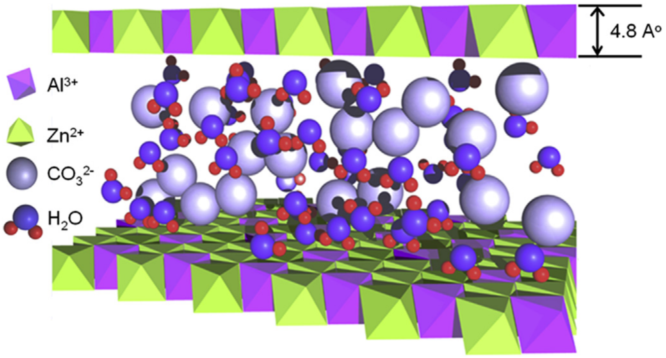

Fig. 1. Schematic presentation of LDH showing edge sharing octahedrons of bi and tri-valent metal ions along with interlayer water and exchangeable carbonate anions. The layer thickness for brucite-like hexagonal LDH is assumed to be 4.8 Å [43,44].

the substrate. In other words, mechanical vibration is a function of crystal structure and infrared spectroscopy is a versatile method for analyzing bonding interactions at the molecular level.

The study of different aspects of structure of hydrotalcites (Ht) has been reported by Raman and infrared spectroscopy. Kloprogge et al. [18] found a small but interesting change in band positions of the modes related to the hydroxyl groups with different Ht. Extensive work on the characterization of Ht by the spectroscopic study has been done by Frost et al. group [19–26].

The effect of different composition of LHDs or Ht (by varying bi and tri-valent metal ions, interlayer anion, modification with different organic anions) on the Raman and infrared spectroscopy has been comprehensively studied. In recent years, a few reports on the characterization of LDHs using Raman and infrared spectroscopy have been reported [24,25,27–29]. These reports mainly concentrate on the characterization of LDHs (or Ht) with different combination of M^{2+} and M^{3+} or modified LDHs with different organic anions.

However, the spectroscopic study of LDH as a function of bi and tri-valent metal ratio remains less understood. It is expected that the band position of different bending (δ) and stretching (ν) modes associated with the different constituent ions (Zn^{2+}, Al^{3+}, OH, CO_3^{2-} in this case) should vary with the cation ratio. As the percentage of Zn^{2+}, Al^{3+}, CO_3^{2-} varies, so does their interactions with each other. The change of band position (if any) with cation ratio may reveal new interesting information regarding the complex structure of LDHs. The only report about the spectroscopic study of a synthetic Ht with a complex octahedral chemistry as a function of different bi and tri valent metal ratio is by Palmer et al. [30].

In the present study, interesting changes in Fourier transform infrared spectra (FTIR) of different synthetic LDH has been identified by band component analysis. Attempt has been made to correlate these changes in the different bands (in terms of peak position and area under the curve) with bi and tri valent metal ratio-obtained from chemical analysis of LDH. The activation of an IR inactive peak in the spectrum has been identified and the effect of metal ratio on this peak is also studied in details. To the best of our knowledge, there is no such report which correlates the evolution and variation of various IR bands with LDHs composition.

2. Experimental details

2.1. Chemicals

All the reagents ($ZnCl_2$, $AlCl_3$. $6H_2O$ and Urea – Merck India Pvt. Ltd.) were used without further purification and all the experiments were performed at room temperature. Ultrapure membrane filtered water (MFW) of conductivity = 18.2 mS, was used in all experiments.

2.2. Synthesis of Zn–Al CO_3 LDH

Zn–Al LDH was synthesized by homogeneous co-precipitation method using urea [31,32]. 10 ml of $AlCl_3 \cdot 6H_2O$ and 30 ml $ZnCl_2$ solution (both 1 M) were mixed together and filtered. To 7 ml of that mixture, 1100 mg urea and 210 ml MFW were added and placed in teflon-coated stainless steel autoclave. The mixture was heated without stirring for 22 h at 120 °C. Then it was cooled to room temperature and washed with hot water several times until it became chloride free. Finally, the powder was dried overnight under vacuum to produce Zn–Al CO_3 LDH of layer charge 0.25. By using the above procedure the other two layers charged materials were synthesized and the batch composition is provided in Table 1.

2.3. Characterization

For chemical analysis ~10 mg of powdered sample was dissolved in 15 ml (N/10) HCl (pH~1) for 2 h (see Table 2). Then an aliquot of this solution was taken to determine the concentration of Zn^{2+} and Al^{3+} ion by inductively coupled plasma atomic emission spectrometer (ICP-AES, Ciros Vision, Spectro Analytical Instruments Inc.). Powder X-ray diffraction analysis of synthesized LDH was carried out by X'Pert Pro diffraction unit (PANalytical) with Ni filtered Cu-K_α radiation. The diffraction pattern was recorded within the angle range $10° < 2\theta < 70°$, where θ = Bragg's angle. Samples were oven dried at 60 °C for 24 h to remove the adsorbed water and stored in a desiccator before FTIR experiment. A small amount of the sample was prepared in pellet form with KBr (sample: KBr ratio was 1:1000) and FTIR was conducted (Frontier FTIR/FIR Spectrometer, PerkinElmer) in 4000 to 400 cm^{-1} range having a spectral resolution of 4 cm^{-1}. Initially FTIR data was acquired without any sample for the background correction followed by the sample in KBr pellet form. Spectral manipulation such as base line adjustment, smoothing (if any) were performed using ORIGIN8 Pro software. Non-linear curve fitting was achieved by the same software using Gauss function and the fitting was well reproducible with a very high correlation coefficient (r^2) value. Particle size analysis was carried out by Dynamic Light Scattering method by dispersing the sample in aqueous medium (Nano Practica SZ100, Horiba). Micro-structural characterization was done by field emission scanning electron microscopy (FESEM), for which a very dilute dispersion (in MFW) of the material was coated with carbon to make the surface conducting. FESEM images were captured by Gemini Zeiss Supra™ 35VP model.

3. Results and discussion

XRD patterns of the synthesized LDHs (Fig. 2) show sharp and symmetrical reflections at lower 2θ values, which are characteristic reflections of Ht -like compounds with high degree of crystallinity. Reflections in the diffractogram can be classified into several basal (*00l*) and non basal reflections (*hk0*) and matches with 2H polytype of LDH (Manasseite, JCPDS 14-525) which can be indexed into P −6 2 m space group. The unit cell parameters were calculated using formula-a = $2d_{110}$ and c = $(2d_{002}+3d_{003}+4d_{004})/3$ and it was around a = b = 3.04 Å, c = 13.73 Å, $\alpha = \beta = 90°$ $\gamma = 120°$. It is known that metal hydroxide layers of LDH consist of close packed hydroxide ions with octahedral cations separated by distance that corresponds to the 110 reflection which appear around $2\theta = 60°$ (i.e., $d_{110} = 1.52$ Å) and can be stacked in several ways to generate various polytypes. The most intense reflection at around $2\theta = 12.68°$, attributed to basal reflection (d_{002}), corresponds to