

Intercalation of Azo Dyes in Ni-Al Layered Double Hydroxides†

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Ni-Al layered double hydroxides were synthesized by hydrothermal process and intercalated with azo dyes *viz.* metanil yellow, sunset yellow and amaranth by anion exchange process. The resulting hybrid intercalated solid compounds were characterized by powder XRD, FTIR, DRS and TGA. The powder X-ray diffraction revealed the presence of supramolecular host-guest interaction between the host matrix and interlayer anionic dye guest with an expanded interlayer distance. The TGA studies showed that the dye-intercalated layered double hydroxides had higher thermal stability than the pristine dye. Moreover, there was no significant change in the UV-VIS/DR spectra of the dye-intercalated sample after heating up to 200 °C, indicating that the thermal stability of dye is markedly enhanced by the intercalation into the gallery domain of NiAl-LDH.

Key Words: Ni-Al LDH, Intercalation, Azo dyes, XRD, TGA.

INTRODUCTION

Inorganic-organic hybrid materials constitute a class of materials, which are presently of considerable interest as they might edifice the properties of their constituents^{1,2}. The controlled supramolecular host-guest assembly of the two components creates new multifunctional systems in which each sub network might exhibit its own properties or might contribute to new physical phenomena and novel applications. In this respect, intercalation of organic host into the layers of double hydroxides has created its own domain by achieving its potential applications, in catalysis and photovoltaics³⁻⁵. The interest stems from the peculiar molecular arrangement imposed by the host structure, the thermal stability supplied by the inorganic constituent and the stability against the dissolution process, the whole contributing to maintain the optical properties of the intercalated dye. Owing to the highly tunable layered double hydroxide interlayer composition coupled with the wide possible choice of anionic organic moiety, a large variety of layered double hydroxide hybrid materials has been reported and several review articles and chapters are devoted to the intercalation chemistry of layered double hydroxides and their applications^{6,7}.

Azo dyes are known for their potential efficiency in non linear optics (second harmonic generation)⁸ and for their ability to photoisomerization⁹⁻¹¹. In the past few years, many researches have been devoted to the synthesis and study of lamellar hybrid

compounds functionalized by dyes because of potential applications in photophysical and photochemical devices. Some important findings were suggested by Costantino and co-workers on chromophores with donor acceptor properties¹², phenolphthalein¹³, methyl orange¹⁴, *etc.* Indeed, these authors have been pioneers in determining whether hydrothermal-type materials were able to intercalate large size dye and in obtaining information on the orientation/ conformation of the dye by measurements of basal spacing and photophysical properties¹⁵.

Following the work of insertion of organic molecules possessing π -electron systems we have chosen three commercially available anionic dyes, metanil yellow (sodium 3-[4-(anilino)phenyl]diazanylbenzenesulfonate), sunset yellow (disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalene-sulfonate) and amaranth (trisodium (4*E*)-3-oxo-4-[(4-sulfonato-1-naphthyl)hydrazono]naphthalene-2,7-disulfonate to incorporate into Ni-Al layered double hydroxides.

EXPERIMENTAL

The materials aluminium nitrate and nickel nitrate used were from LOBA CHEMIE, sodium hydroxide and sodium carbonate were procured from Fine Chemicals Limited, metanil yellow, sunset yellow and amaranth used were from SIGMA Aldrich.

Synthesis of layered double hydroxide: A mixture of Ni(NO₃)₂·6H₂O and Al (NO₃)₃·9H₂O was dissolved in 30 mL deionized water to form a clear solution ([Ni²⁺] = 0.2 M, [Al³⁺]

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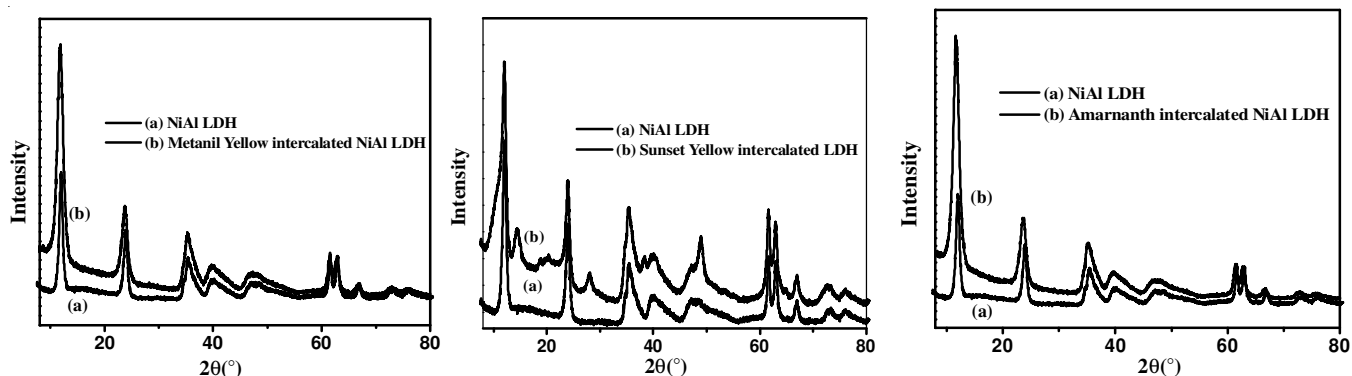


Fig. 1. PXRD of NiAl layered double hydroxide (LDH) and metanil yellow, sunset yellow, amaranth intercalated NiAl LDH

TABLE-1
PXRD AND SURFACE AREA OF NiAl LAYERED DOUBLE HYDROXIDES (LDH) AND INTERCALATION OF METANIL YELLOW, SUNSET YELLOW AND AMARANTH WITH NiAl LDH

Compound	d-spacing	HKL	Pore volume (cm ³ /g)	Surface area (m ² /g)
NiAl LDH	7.9	003	0.044	106
Metanil yellow intercalated NiAl LDH	8.8	003	0.134	161
Sunset yellow intercalated NiAl LDH	8.7	003	0.088	146
Amaranth intercalated NiAl LDH	8.9	003	0.204	178

= 0.1 M). The salt solution was rapidly poured into a 30 mL NaOH and Na₂CO₃ solution ([OH⁻] = 0.48 M, [CO₃²⁻] = 0.2 M) under vigorous stirring. The mixture was further stirred for 20 min at room temperature. Subsequently, the suspension was centrifuged, washed and redispersed in deionized water for 5 cycles to remove residue salts. The resulting precipitate was transferred into a 100 mL Teflon-lined stainless steel autoclave with 70 mL deionized water. The autoclave was then tightly sealed and heated in an oven at 423 K for 10 h. The resulting bluish green suspension was dried in an oven at 343 K.

Intercalation: 1 g of layered double hydroxide was added to an aqueous solution of 0.5 g of sunset yellow in 70 mL of decarbonated water. Then the solution was stirred for 72 h. The solid was centrifuged, washed and redispersed in deionized water for 5 cycles and the light yellow solid was dried in an oven at 338 K. Similarly, we have also intercalated Metanil Yellow and Amaranth in NiAl layered double hydroxide.

Ni and Al were estimated by gravimetric Method [20], the C, H and N analysis was done with a PERKIN ELMER 2400 Analyzer. Powder X-ray diffraction (PXRD) were collected on a Bruker D₈ advance X-ray diffraction measurement system at USIC, GU. Fourier transform infrared spectra (FT-IR) were recorded in a Perkin-Elmer spectrum RX/FTIR system, TGA was measured in a METTLER TOLEDO instrument in nitrogen atmosphere at a heating rate of 10 °C/min. The diffuse reflectance spectra of the samples were recorded in a HITACHI, U-4100 spectrophotometer. Specific surface area (BET) were measured with N₂ adsorption/desorption in a Micromeritic Triastar 3000 apparatus. HRTEM images were recorded in a JEOL JEM-2100 Electron Microscope.

RESULTS AND DISCUSSION

Powder XRD: The XRD patterns for the Ni-Al layered double hydroxides and the dye intercalated layered double hydroxide are shown in Fig. 1. The peaks corresponds to the (003) (006) (012) (110) and (113) reflections of layered double

hydroxide. The values obtained are in good agreement with the literature data. The d value corresponding to 003 reflections are given in the Table-1. A closer examination of the XRD patterns for these organic-substituted systems revealed a broadening and shifting of some fundamental layered double hydroxide reflections. These results suggest that the organic guest anions fit well within the interlayer galleries of Ni-Al layered double hydroxide¹⁶⁻¹⁹.

FTIR analysis: The FTIR spectra of the layered double hydroxides and pure organic inhibitor powders are shown in Fig. 2. The layered double hydroxide samples show broad bands in the range of 3500-3400 cm⁻¹ due to the stretching mode of structural OH groups in the metal hydroxide layer, similar broad peak were also observed in the pure azodyes due to some moisture adsorption. In the case of carbonate-loaded layered double hydroxides, a peak occurring at 1600 cm⁻¹ can be ascribed to the bending mode of interlayer water molecules. Additionally, an intensive peak occurring at ca. 1365 cm⁻¹, corresponds to symmetric stretching modes of carbonate. The broad peaks below 1000 cm⁻¹ can be assigned to Ni²⁺ - OH or Al³⁺ - OH bending modes. Following the exchange of CO₃²⁻ by sunset yellow anion, the peak at 1365 cm⁻¹ significantly decreases and several new peaks appear in the corresponding FTIR spectrum. A comparison between the FTIR spectra of Ni-Al-intercalated with sunset yellow dye and pure sunset yellow azo dye allows one to conclude that these new peaks can be assigned to different vibration modes of intercalated dye anions. Furthermore, variation of the peak positions and intensities may be indicative of the interaction between the intercalated organic anions and the positively charged hydroxide layers. Sunset yellow intercalated NiAl layered double hydroxide, band at 1591 cm⁻¹ due to C C stretching mode of benzene, 1387 cm⁻¹ due to azo stretching vibration, 1213 cm⁻¹ due to C-N stretching vibration, 1211 cm⁻¹ due to SO₃ stretching vibration, 643 cm⁻¹ due to SO₃ bending vibration. The same trend was found for layered double

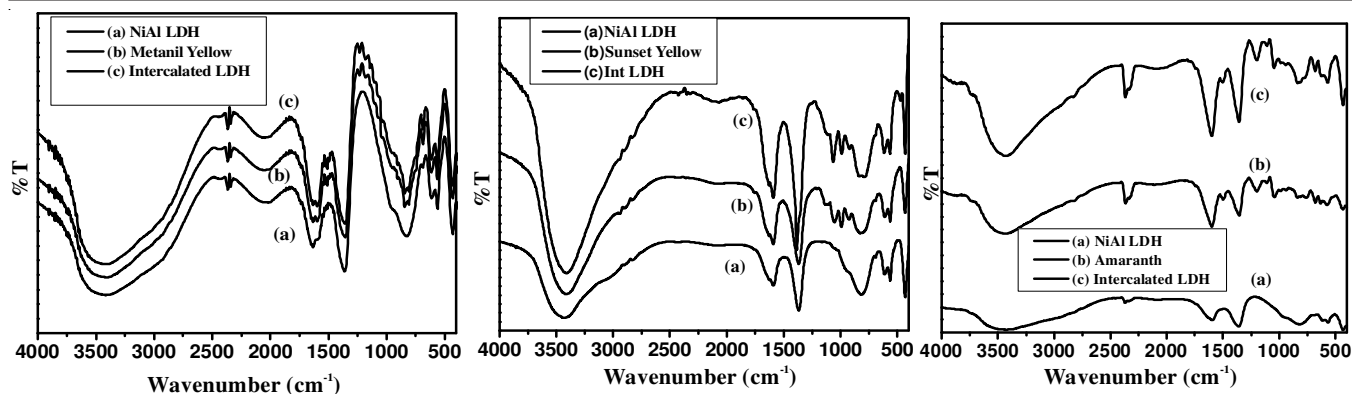


Fig. 2. FTIR of NiAl layered double hydroxide (LDH) and metanil yellow, sunset yellow, amaranth intercalated NiAl LDH

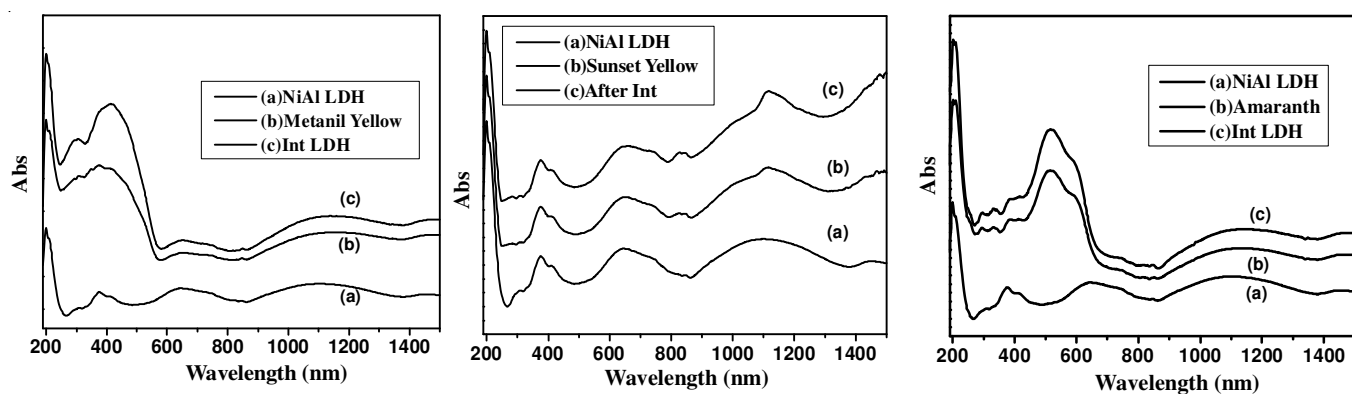


Fig. 3. DRS of NiAl LDH and metanil yellow, sunset yellow, amaranth intercalated NiAl LDH

hydroxides loaded with other two dyes. These results clearly indicate the successful ion exchange of carbonate anions by organic anions, leading to the creation of new nanocontainers. Metanil Yellow and Amaranth intercalated NiAl layered double hydroxide, the bands were shown at 1211 cm^{-1} due to SO_3 stretching vibration, 643 cm^{-1} due to SO_3 bending vibration.

UV-VIS/diffuse reflectance spectra: The diffuse reflectance spectrum of Ni-Al layered double hydroxide is shown in Fig. 3). It shows five absorption peaks nearly at 205, 376, 417, 645 and 1105 nm. The peak at 205 and 376 nm can be assigned to charge transfer transitions originated from a transition from oxygen-to Ni^{2+} and Al^{3+} of layered double hydroxide moiety. The peak at 417 and 645 nm can be attributed to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions of octahedral Ni-hydroxo complex in the layered double hydroxide. Comparison with Ni model compounds showed that the band at 417 is a unique fingerprint of $\text{a-Ni}(\text{OH})_2$ and the band at 645 to Ni-Al layered double hydroxide. The neat sunset yellow dye shows three spectral bands in the regions 207, 283 and 361 nm. Similarly the other two dyes before intercalation shows bands at 316, 338 and 421 nm for metanil yellow and 207, 294, 326, 510 nm for amaranth. In all the three case the peaks at lower wavelength can be attributed to the $\pi \rightarrow \pi^*$ transitions whereas those in the higher wavelength are due to $n \rightarrow \pi^*$ transitions. After intercalation into the Ni-Al layered double hydroxide, in case of sunset yellow the higher energy bands are blue shifted whereas the lower energy bands are red shifted. And a new peak at 825 nm region is observed which may be due to electronic transition results from the presence of the

Ni^{2+} in the layered double hydroxide moiety. The values for the electronic transitions are provided in after intercalation of metanil yellow into layered double hydroxide, the higher energy bands are found to be shifted into blue region while two new peaks are found to be shifted into higher wavelength. Similar kind of change is also observed after intercalation of amaranth. The appearance of few new peaks at higher wavelength in all the cases further confirms that the azo dyes are successfully intercalated into the layers of Ni-Al layered double hydroxide. However, due to columbic interaction that occurs between the negatively charged azo dyes and positive charge that originated in the lattice of layered double hydroxide results in the blue and red shifting of the lower and higher energy bands.

HRTEM: The HRTEM shows the layer lattice structure of NiAl layered double hydroxide. The Fig. 4 shows the morphology of the NiAl layered double hydroxide and metanil yellow, sunset yellow and amaranth intercalated NiAl layered double hydroxide. The TEM image shows rod like layers for NiAl layered double hydroxide and honey-comb structures for the intercalated layered double hydroxide.

Surface area: The BET surface area calculated by from N_2 adsorption/desorption isotherm $106\text{ m}^2/\text{g}$ for NiAl layered double hydroxide and for intercalated metanil yellow, sunset yellow and amaranth layered double hydroxide were 161, 146, $178\text{ m}^2/\text{g}$ respectively. The micropore volume determined by BJH method was $0.044\text{ cm}^3/\text{g}$ for layered double hydroxide and $0.088\text{ cm}^3/\text{g}$ for intercalated layered double hydroxide. The slight increase of surface area and pore volume on intercalations of larger anion in place of carbonate increases the interlayer space of hydroxide layers.

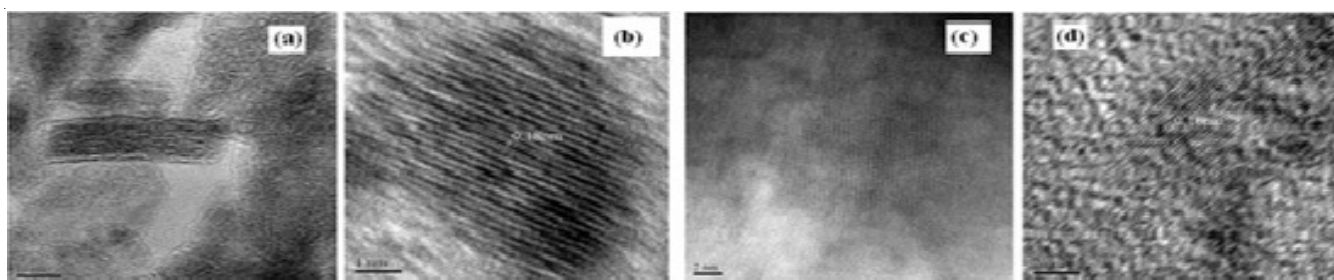


Fig. 4. HRTEM of (a) NiAl LDH and intercalation of (b) metanil yellow (c) sunset yellow (d) amaranth with NiAl LDH

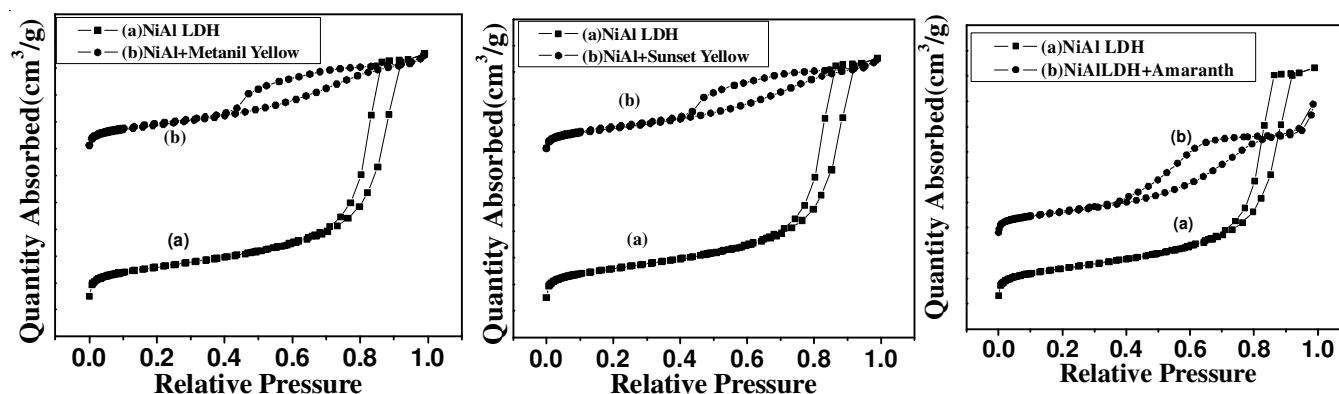


Fig. 5. Surface area of NiAl layered double hydroxide (LDH) and metanil yellow, sunset yellow, amaranth intercalated NiAl LDH

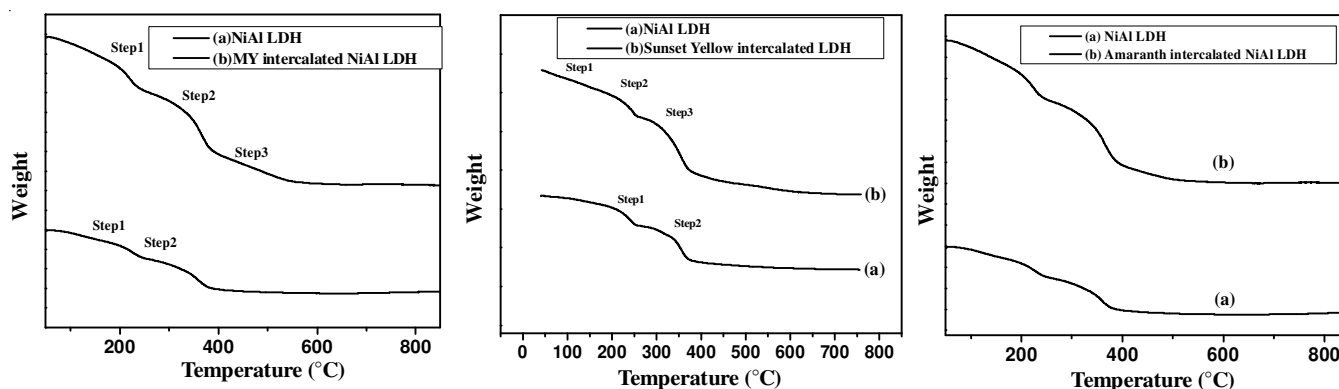


Fig. 6. TGA of NiAl LDH and metanil yellow, sunset yellow, amaranth intercalated NiAl LDH

Thermal decomposition: The thermogravimetric analysis for Ni-Al CO_3 layered double hydroxide and metanil yellow, sunset yellow and amaranth intercalated NiAl layered double hydroxide were shown in Fig. 6. The Ni-Al-layered double hydroxide with carbonate anions show two weight losses. The first weight loss at 383-513 K was due to loss of interlayer water and second weight losses at 533-623 K were due to decarboxylation and dehydroxylation. The Ni-allayered double hydroxide intercalated with sunset yellow show three weight losses at 383-513, 533-553 and 713-793 K. The first two weight losses were due to loss of hydrocarbons of the aromatic moiety present in the sunset yellow azo dye. The second weight loss is due to the breaking of dye linkages. The third weight at slightly higher temperature was due the loss of sulphate anions. Similar kind of TGA pattern was also observed in case of the layered double hydroxides intercalated with metanil yellow and amaranth (azo dyes). The comparison of the TGA pattern with that of pristine dye indicate that intercalation enhances

the thermal stability of these azo dyes and hence can be used without any prior thermal treatment in photovoltaic devices and catalysis.

Conclusion

We have successfully prepared NiAl layered double hydroxide *via* hydrothermal process and intercalated layered double hydroxide with metanil yellow, sunset yellow and amaranth *via* anion exchange process. Intercalation of NiAl layered double hydroxide with sunset yellow resulted in light yellow coloured microcrystalline product with basal spacing of 7.9 Å to 8.77 Å, as evidenced by PXRD. The intercalation leads to the blue shifting and red shifting of the electronic transitions of the azo dyes. Intercalation has led to the increase in the thermal stability of these dyes. The surface area after intercalation are found to be more for which these materials can be further treated as catalyst and apply them in photovoltaic designing.

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