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Preparation of an anionic azo pigment-pillared layered double hydroxide and the thermo- and photostability of the resulting intercalated material

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Abstract

A large anionic pigment has been intercalated into a layered double hydroxide (LDH) host by ion-exchange of an Mg/Al LDH-nitrate precursor with a solution of C.I. Pigment Red 48:2 (the calcium salt of 4-((5-chloro-4-methyl-2-sulfophenyl)azo)-3-hydroxy-2-naphthalene-carboxylic acid), in ethane-1,2-diol. After intercalation of the pigment, the interlayer distance in the LDH increases from 0.86 to 1.72 nm. Infrared spectra and TG–DTA curves reveal the presence of a complex system of supramolecular host–guest interactions. The UV-visible diffuse reflectance spectra of C.I. Pigment Red 48:2 show marked changes after heating at 200 °C and above, whereas there are no significant changes in the spectra of the intercalated pigment after heating at temperatures up to 300 °C, showing that the thermostability is markedly enhanced by intercalation in the LDH host. The pigment-intercalated LDHs exhibits much higher photostability to UV light than the pristine pigment, in the case of both the pure solids and their composites with polypropylene, as shown by measurement of CIE 1976 $L^*a^*b^*$ color difference (ΔE) values.

Keywords: Hydrotalcite; Azo pigment; Intercalation; Thermostability; Photostability

1. Introduction

Plastics and coatings may be colored by incorporation of either inorganic pigments [1] or organic dyes and pigments [2]. The former have high UV, oxygen and thermal stability but mainly involve heavy metals, which may lead to environmental problems during processing or recycling and exhibit a limited range of color shades and low brilliance. Organic materials are more environmentally friendly and may be synthesized with a wide range of brilliant shades but suffer from limited UV and/or oxygen and thermal stability. There has been considerable work on intercalation of cationic dyes in zeolites [3], aluminosilicate clays [4] and metal (IV) phosphonates [5]. This should have the effect of stabilizing the dye against UV, oxidative or thermal degradation and give a superior type of pigment. Such materials also have potential applications as nonlinear optical materials provided that they have sufficient thermal and optical stability under relatively strong laser irradiation [6]. The majority of dyes however are anionic and cannot be intercalated into clays or metal (IV) phosphonates.

Layered double hydroxide (LDH) materials, also called hydrotalcite-like compounds, represent an alternative class of clay-type materials [7]. LDHs are the one of the very few types of inorganic materials with positively charged layers, which allows the interlayer anions in simple LDH precursors to be replaced by other anions to form a large number of new functional materials [8]. The general formula of LDHs is $\left[M^{\mathrm{II}}_{1-x}M^{\mathrm{III}}_{x}(\mathrm{OH})_2^{x+}\right]\cdot\left[A^{n-}_{x/n}\right]^{x-} m\mathrm{H_2O}$, where M^{II} and

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M^{III} are divalent and trivalent metal cations, respectively, x represents the molar fraction of M^{III} cation; A^{n-} is the charge compensating anion; and m is the number of water molecules located in the interlayer region together with anions. They have been extensively studied as catalysts, catalyst supports, pharmaceuticals, anionic exchangers, adsorbents and polymer additives [9].

Several examples of the intercalation of water-soluble sulfonated organic dyes in LDHs have been reported in the literature [10,11]. The dyes may be slowly leached from the host however [10d] and the stability to light and heat of the resulting intercalated materials has not generally been investigated. In the one case where the photostability of pristine and LDH-intercalated pigments has been compared (for perylene bisimidetetrasulfonate), it was found [11] that intercalation afforded no significant advantage. Indeed, when the pigments were included in cement, the photostability of the LDH-intercalated pigment was found to be lower than that of the pure pigment. To the best of our knowledge, investigation of the stability of LDH-intercalated pigments as components of polymer composites has not been reported in the literature.

The BON group of pigments consists of monoazo pigment lakes (water-insoluble metal sulfonate salts) based on 2-hydroxy-3-naphthoic acid [12]. They are widely used in printing inks and paints and other coatings as their calcium, barium or manganese salts. The manganese salts are generally more lightfast than the corresponding alkaline-earth salts but are seldom used as pigments for plastics because manganese catalyzes the oxidative decomposition of the polymer. It would be desirable therefore to develop a method of enhancing the stability of the pigment without incorporation of transition metal ions. In this work we report the intercalation of one representative member of this class of materials, C.I. Pigment Red 48:2 (the calcium salt of 4-((5-chloro-4-methyl-2-sulfophenyl)azo)-3-hydroxy-2-naphthalene-carboxylic acid), in an Mg/Al LDH and a comparison of the thermal and optical stability of the resulting materials with that of the pristine pigment. The structure of the azo dye anion and its keto-hydrazone tautomer are shown in Fig. 1.

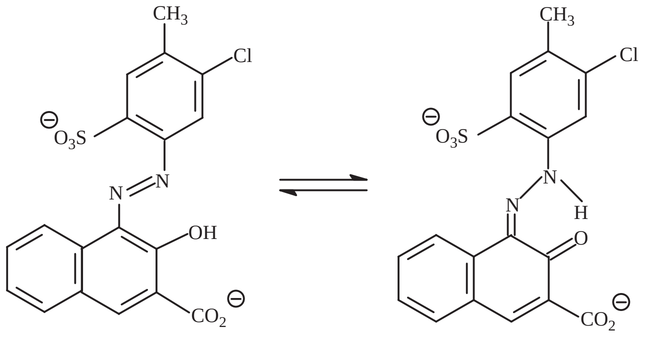

Fig. 1. Structure of the two tautomeric anions of C.I. Pigment Red 48:2 (the calcium salt of 4-((5-chloro-4-methyl-2-sulfophenyl)azo)-3-hydroxy-2-naphthalene-carboxylic acid).

2. Experimental

2.1. Materials

C.I. Pigment Red 48:2 (technical grade, 99 wt%) was directly used without purification. The conductivity of deionized water used to synthesize and wash samples was less than 10^{-6} S/cm. Other reagents used in this work were all A.R. grade.

2.2. Preparation of Mg/Al–NO_3 LDH precursor

All solutions were prepared using deionized water which had been previously decarbonated by boiling and saturating with N_2. $Mg(NO_3)_2 \cdot 6H_2O$ (15.4 g, 0.06 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (11.3 g, 0.03 mol) were dissolved in CO_2-free deionized water (50 mL) to make a mixed salt solution. NaOH (7.20 g, 0.18 mol) was dissolved in CO_2-free deionized water (75 mL) to make an alkali solution. Under the protection of an N_2 stream, the two solutions were simultaneously added to a colloid mill [13] rotating at 3000 rpm and mixed for 2 min. The resulting slurry was then aged at 65 °C for 39 h. After centrifugation and extensive washing, the precipitates were squeezed between filter paper to give a cake containing 15.1 wt% of solid. A portion of the filter cake was dried at 70 °C for 24 h. Analysis %: Found (calc. for $Mg_{0.66}Al_{0.34}(OH)_2(NO_3)_{0.34} \cdot 0.37H_2O$) Mg 18.14 (18.26); Al 10.31 (10.58).

2.3. Assembly of C.I. pigment red 48:2 anion-pillared LDH

A portion of the Mg/Al–NO_3 LDH filter cake (ca. 1.86 g dry solid, ca. 7.3 mmol NO_3^-) was suspended in ethane-1,2-diol (35 mL) with stirring. A solution of C.I. Pigment Red 48:2 (2.32 g, 5.06 mmol) in hot ethane-1,2-diol (100 mL) was added under nitrogen. The mixture was stirred under nitrogen for 48 h at 90 °C. The resulting precipitate was centrifuged, thoroughly washed with portions of hot ethane-1,2-diol until the washings were colorless and then subsequently washed with water and dried in an oven at 70 °C for 24 h. Analysis %: Found (calc. for $Mg_{0.66}Al_{0.34}(OH)_2(C_{18}H_{11}ClN_2O_6S)_{0.17} \cdot 1.42H_2O$) Mg 10.85 (10.17); Al 6.32 (5.89); N 2.99 (3.06); S 3.84 (3.49); Ca < 0.05.

A sample of the pigment (0.2 wt%) was thoroughly mixed with polypropylene powder and the mixture molded into plates ($50 \times 50 \times 3\ mm^3$) in an SZA-YY-60 injection molding machine at 200 °C.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were obtained using a Shimadzu XRD-6000 diffractometer with monochromatic Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å) operating at 40 kV and 20 mA, with a step size of 0.02° 2θ. Infrared (IR) spectra were recorded on a Bruker Vector 22 Fourier transfer infrared spectrophotometer using the KBr disk method with a ratio of sample/KBr of 1:100 by mass. Thermogravimetry and differential thermal analysis (TG–DTA) curves were recorded on a Setaram PCT-IA instrument in the temperature range 40–600 °C with a heating rate of 10 °C/min in flowing air. The samples were dried at 70 °C prior to the measurements. Diffuse reflectance UV-visible absorbance spectra were recorded using a Shimadzu UV-2501PC instrument with an integrating sphere attachment in the range 200–800 nm using $BaSO_4$ as reference. Elemental analysis was carried out by X-ray fluorescence using a Shimadzu XRF-1700 instrument.

The color difference (ΔE) of materials aged under UV light ($\lambda_{max} = 365$ nm) was determined using the CIE 1976 $L^*a^*b^*$ method [14] using a TC-P2A automatic colorimeter and color difference meter (Xinao Yike Optic-Electronic Co., Beijing). A ΔE reading of 0 represents a perfect match. A value of 1 is supposed to represent the smallest variance the human eye can see, although the sensitivity of the eye is not uniform across the spectral range. In the case of red pigments, color differences of $<\Delta E \sim 2.2$ are indistinguishable from one another [15].

2.5. Theoretical calculations

These were carried out at the restricted Hartree-Fock level using the PM3 semi-empirical SCF-MO method as implemented in the Gaussian 03 package [16]. The molecular geometries were optimized using analytical gradients optimization routines.

3. Results and discussion

3.1. Structure of the samples

XRD patterns of the Mg/Al–NO_3 LDH precursor, C.I. Pigment Red 48:2, and the product of an excess of a solution of the pigment in ethane-1,2-diol with an aqueous suspension of the LDH are shown in Fig. 2. The X-ray diffraction pattern of the LDH precursor (Fig. 2a) exhibits the characteristic pattern of a layered solid with sharp, symmetrical peaks at low angle corresponding to the basal reflection and higher order reflections, and some asymmetrical peaks at high angle. The basal spacing (d_{003}) of the LDH is 0.86 nm. Xu and Zeng [17] have demonstrated that the value of the basal spacing for nitrate-containing LDHs is very sensitive to the NO_3^- content which is a function of the Mg^{2+}/Al^{3+} ratio. Values of $d_{003} < 0.82$ nm are associated with low nitrate content, and in such materials the nitrate anions lie in the center of the interlayer galleries. Values of $d_{003} > 0.82$ nm are characteristic of high nitrate content and it has been suggested that nitrate anions are alternatively associated with upper and lower metal-hydroxide layers in order to relieve steric crowding [17]. The basal spacing of our LDH (Mg^{2+}/Al^{3+} ratio of ca. 2) is consistent with this interpretation. The single crystal structure of a chlorinated derivative of C.I. Pigment Red 48:2 has recently been reported and shown to involve a complex supramolecular structure [18]. The powder X-ray diffraction pattern of C.I. Pigment Red 48:2 (Fig. 2b) confirms that the sample is microcrystalline. By design, pigments such as C.I. Pigment Red 48:2 are insoluble in water, so the reaction of the LDH-nitrate precursor was carried out using a suspension of the solid in a solution of C.I. Pigment Red 48:2 in ethane-1,2-diol at 90 °C. After reaction, the basal spacing of the LDH increased to 1.72 nm (Fig. 2c), indicating that the anionic pigment had been intercalated between the layers. The absence of any reflections due to the LDH-nitrate precursor suggests that intercalation is complete and the absence of any reflections arising from the pure pigment indicate that

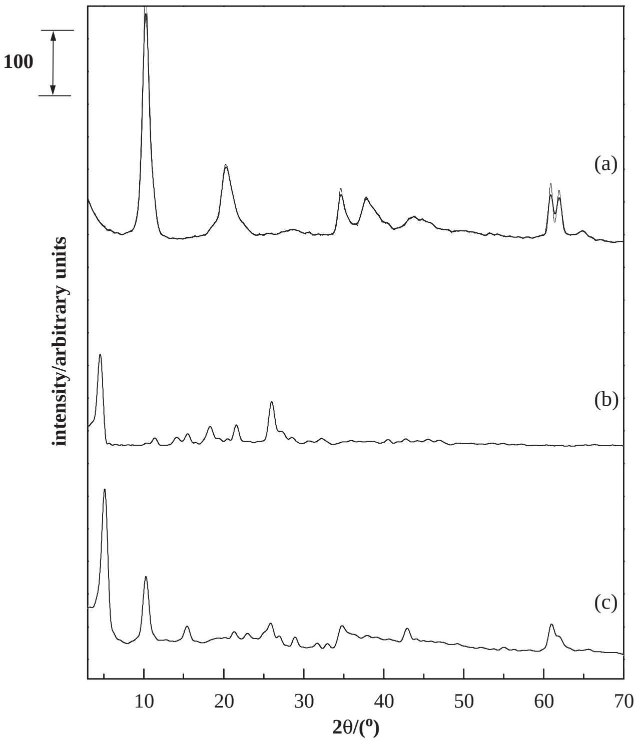

Fig. 2. X-ray diffraction patterns of: (a) Mg/Al-NO_3 LDH, (b) C.I. Pigment Red 48:2, and (c) C.I. Pigment Red 48:2 anion-pillared LDH. Intercalation of the pigment in the LDH leads to a large increase in basal spacing.

it has not been adsorbed on the surface of the LDH to any significant extent. Given that the thickness of the layers in LDHs is 0.48 nm [8], the interlayer spacing of the pigment-pillared LDH corresponds to a gallery height of 1.24 nm.

Analytical data of the C.I. Pigment Red 48:2 intercalate are consistent with the formulation $Mg_{0.66}Al_{0.34}(OH)_2(C_{18}H_{11}ClN_2O_6S)_{0.17} \cdot 1.42H_2O$. The Mg^{2+}/Al^{3+} ratio is the same as that in the LDH nitrate precursor (1.94). The analytical data suggest that the dianion of the pigment has completely replaced the nitrate ions in the interlayer galleries of the LDH. The calcium content of the material as measured by X-ray fluorescence is below the detection limit ($<0.05\%$), confirming that although the solubility of the calcium salt pigment in ethane-1,2-diol is relatively low it has not been coprecipitated with the LDH phase or adsorbed on the surface.

3.2. *Host–guest interactions*

The FT-IR spectra of C.I. Pigment Red 48:2, Mg/Al–NO_3 LDH, and the product of the reaction of their reaction are shown in Fig. 3. The spectrum of the LDH-nitrate precursor (Fig. 3a) shows the characteristic strong sharp band of the ν_3 stretching vibration of the NO_3^- ion at 1380 cm^{-1} [19]. The FT-IR spectrum of C.I. Pigment Red 48:2 (Fig. 3b) shows the characteristic υ_{as} and υ_s carboxylate stretching vibrations at 1549 and 1407 cm^{-1}, respectively, and bands arising from the sulfonate group vibrations at 1183 and 1039 cm^{-1}. In the spectrum of the C.I. Pigment Red 48:2 anion-pillared LDH (Fig. 3c), the peak characteristic of NO_3^- is absent confirming that the nitrate has been completely replaced by the anionic pigment. The vibrations of the carboxylate and sulfonate groups are clearly apparent, although their positions are slightly shifted from their positions in the calcium salt pigment precursor. In the case of the carboxylate group, the difference $\Delta\nu = \upsilon_{as} - \upsilon_s$ gives information about its coordination environment [20]. Unidentate carboxylate groups exhibit $\Delta\nu$ values of >200 cm^{-1}; bridging carboxylate groups have $\Delta\nu$ values of ~ 150 cm^{-1}; bidentate chelate carboxylate complexes have $\Delta\nu$ values of <100 cm^{-1}. The values of $\Delta\nu$ for the calcium salt C.I. Pigment Red 48:2 and its LDH-intercalate are 142 and 160 cm^{-1}, indicative of a bridging orientation. This is consistent with the structure [14] of the chlorinated analogue of C.I. Pigment Red 48:2, which has calcium ions bridged by anions and suggests that in the case of the LDH-intercalate the carboxylate groups bridge adjacent hydroxyl groups of the layers by means of strong hydrogen bonds.

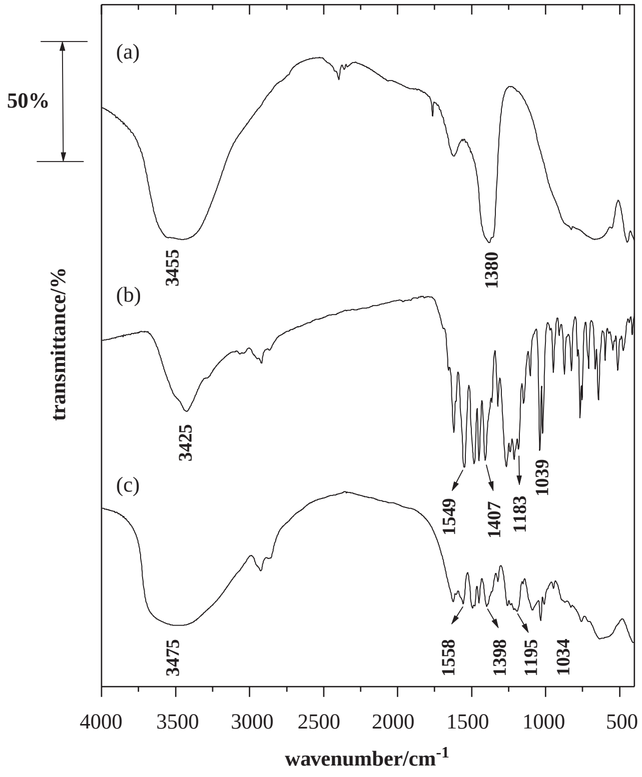

Fig. 3. FT-IR spectra of: (a) Mg/Al-NO_3 LDH, (b) C.I. Pigment Red 48:2, and (c) C.I. Pigment Red 48:2 anion-pillared LDH.

The TG–DTA curves of Mg/Al–NO_3 LDH, C.I. Pigment Red 48:2 and the C.I. Pigment Red 48:2 anion-pillared LDH are shown in Fig. 4. For the Mg/Al-NO_3 LDH precursor the TG curve (Fig. 4a) shows three weight loss steps, with three corresponding endothermic processes in its DTA curve which relate to the desorption of absorbed water at around 153 °C, the dehydroxylation of the brucite-like layer at 353 °C as well as the decomposition of nitrate ions at 400 °C, similar to reports in the literature [13]. The C.I. Pigment Red 48:2 calcium salt begins to lose weight around 200 °C and shows a rapid weight loss in the temperature range 370–450 °C with a corresponding exotherm in the DTA curve at around 385 °C which can be attributed to combustion of the organic material. After the intercalation of C.I. Pigment Red 48:2 into the LDH host, the thermal decomposition characteristics of the resulting product are significantly different from those of the precursors. Liberation of adsorbed water from the interlayer galleries of the intercalate results in an endothermic peak at 235 °C in the DTA curve, approximately 80 °C higher than the corresponding peak for the Mg/Al–NO_3 LDH precursor indicating that the water is more strongly bound in the interlayer galleries after intercalation of the pigment. The amount of water incorporated in the pigment-intercalated LDH according to the TG data is approximately 16.7%, which compares well with a calculated value for $Mg_{0.66}Al_{0.34}(OH)_2(C_{18}H_{11}ClN_2O_6S)_{0.17} \cdot 1.42H_2O$ of 16.1%. The amount of water is significantly higher than that in the Mg/Al–NO_3 LDH precursor which may reflect the larger space available in the expanded

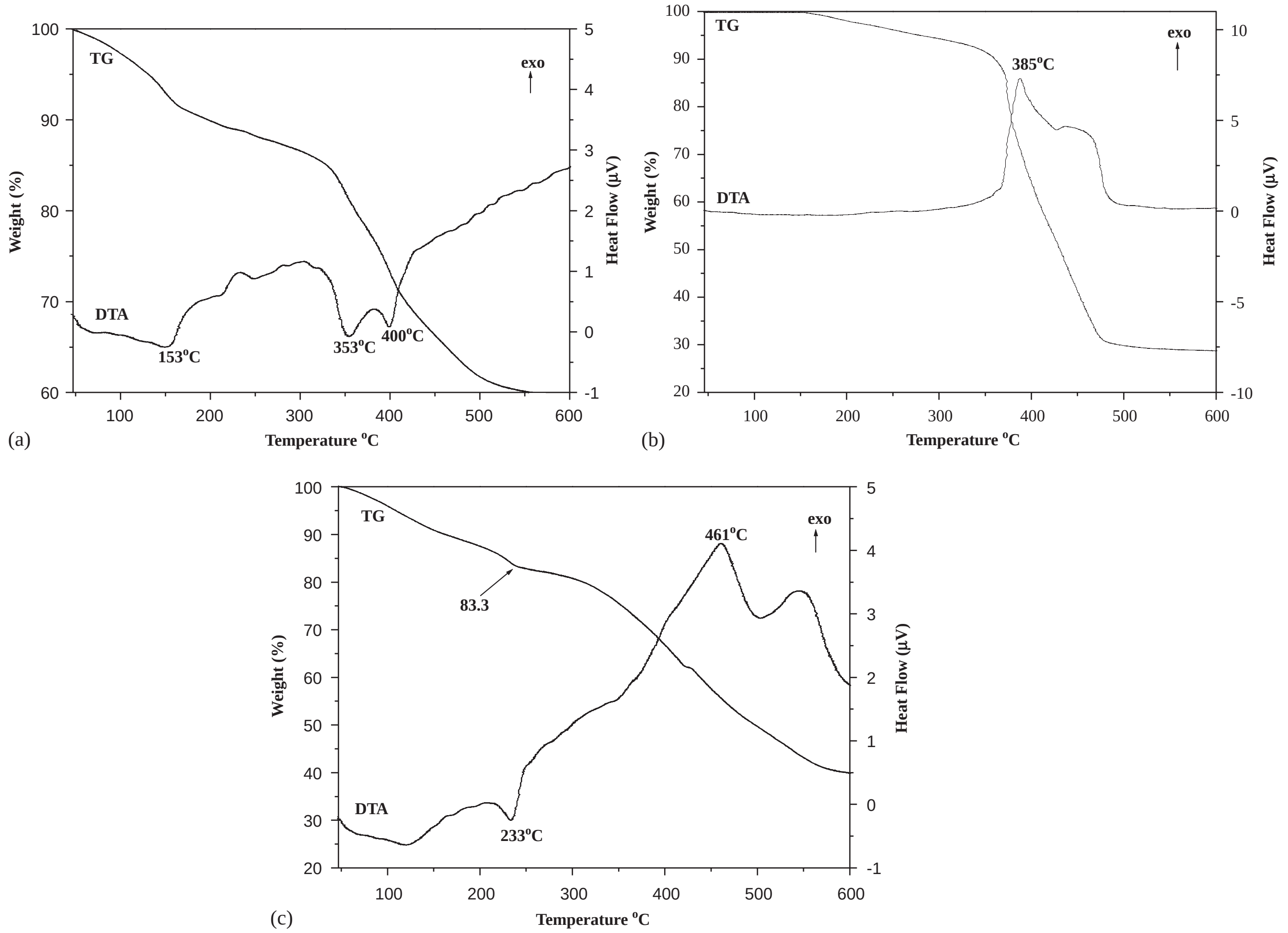

Fig. 4. TG and DTA curves for: (a) Mg/Al–NO_3 LDH, (b) C.I. Pigment Red 48:2, and (c) C.I. Pigment Red 48:2 anion-pillared LDH. Intercalation of the pigment into the LDH host leads to considerable differences in its thermal decomposition process.

interlayer galleries as well as possibility of hydrogen bonding between water molecules and the heteroatoms of the pigment. At higher temperatures, dehydroxylation of the layers overlaps with combustion of the pigment anions and the DTA curve shows two exothermic peaks at 461 and 550 °C. These data suggest that the thermal stability of the pigment is enhanced by intercalation between the layers. This is consistent with the presence of a strongly hydrogen bonded network in the interlayer galleries involving the hydroxyl groups of the layers, the heteroatoms in the pigment as well as interlayer water molecules.

From the differences between the infrared spectra and TG–DTA curves of pristine and intercalated C.I. Pigment Red 48:2, it can be inferred that the intercalated materials have a supramolecular structure with significant host–guest interactions which modify the properties of the organic guest. On the basis of single crystal X-ray diffraction, C.I. Pigment Red 48:2 and related calcium salts are known [14] to exist largely as the keto-hydrazone tautomer (see Fig. 1) in which the carboxylate, sulfonate and keto groups are all coordinated to calcium. Both $-N{=}N-$ and $>C{=}N-$ vibrations give rise to weak IR absorption bands which makes it difficult to determine spectroscopically which tautomer is present in the absence of coordination to calcium, but PM3 semi-empirical SCF-MO calculations have shown [21] that for related uncomplexed azo dyes the phenoxy-azo tautomer is energetically more favorable. We have carried out calculations at the PM3 level on the anion of C.I. Pigment Red 42 and find that the phenoxy-azo tautomer is also energetically favored over the keto-hydrazone tautomer in this case. The calculated N–N and C–N distances of 0.124 and 0.143 nm, respectively, are close to the values expected for $N{=}N$ double bonds and C–N single bonds. The phenoxy hydrogen may engage in intramolecular hydrogen bonding to either the carboxylate oxygen (calculated $H\cdots O$ distance 0.185 nm) or azo nitrogen (calculated $H\cdots N$ distance 0.171 nm) with the latter being slightly more stable in the free anion. The IR data discussed above suggest that the carboxylate group bridges adjacent hydroxyl groups of

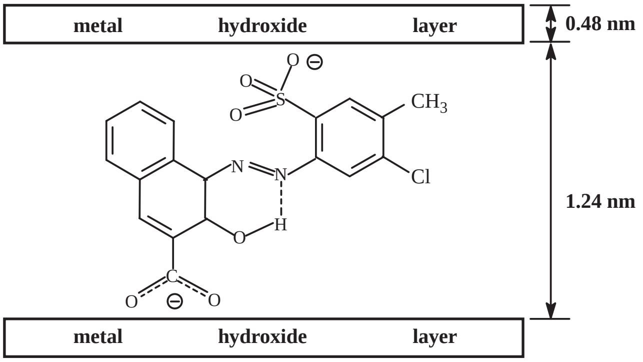

Fig. 5. Possible arrangement of C.I. Pigment Red 48:2 anions in the interlayer region of the LDH host.

the layers by means of strong hydrogen bonds and the sulfonate group is presumably hydrogen bonded to the opposite layer. Since this arrangement precludes an interaction of the keto group with the layers, we believe the phenoxy-azo tautomeric arrangement of the interlayer anion will be favored with an intramolecular hydrogen bond between phenoxy hydrogen and azo nitrogen rather than carboxylate oxygen, since the latter is strongly hydrogen bonded to the layers. A possible arrangement of the ions in the interlayer region is shown in Fig. 5. On the basis of the calculated structure the gallery height is estimated to be 1.21 nm, similar to the experimental value (1.24 nm) determined from XRD data.

3.3. *Thermostability and photostability of C.I. pigment red 48:2 and C.I. pigment red 48:2 anion-pillared LDH*

Samples of C.I. Pigment Red 48:2 and C.I. Pigment Red 48:2 anion-pillared LDH were heated in an oven at 100, 150, 200, 250, 300 °C for 30 min. Diffuse reflectance UV-visible spectra of the resulting solids are shown in Fig. 6. The spectrum of C.I. Pigment Red 48:2 shows significant changes after heating at 200 °C and above. This is consistent with the TG data (Fig. 4b) which shows onset of decomposition around this temperature. The increase in absorption with temperature is most marked in the range 600–700 nm. For azo dyes in solution, photolytic breakdown of the azo chromophore is associated [22] with the formation of decomposition products absorbing in the range 580–680 nm, suggesting that similar products are formed on thermal decomposition of the solid pigment. In the case of the pigment-pillared LDH however, there is no significant change in the spectrum after heating at temperatures below 300 °C, showing that the thermostability of C.I. Pigment Red 48:2 is markedly enhanced by intercalation in the LDH host. This is consistent with the TG data shown in Fig. 4c which indicate that decomposition of the intercalated pigment only begins around 300 °C. The thermal stability of an intimately ground physical mixture of the pigment and the Mg/Al–NO_3 LDH (with the same proportion of pigment as in the intercalate) was also examined. As shown in Fig. 6c, the thermal stability of the mixture is comparable to that of the free pigment and far inferior to that of the intercalated pigment. This demonstrates that the increase in thermal stability of the pigment is indeed associated with intercalation in the interlayer galleries rather than arising from dilution or other effects.

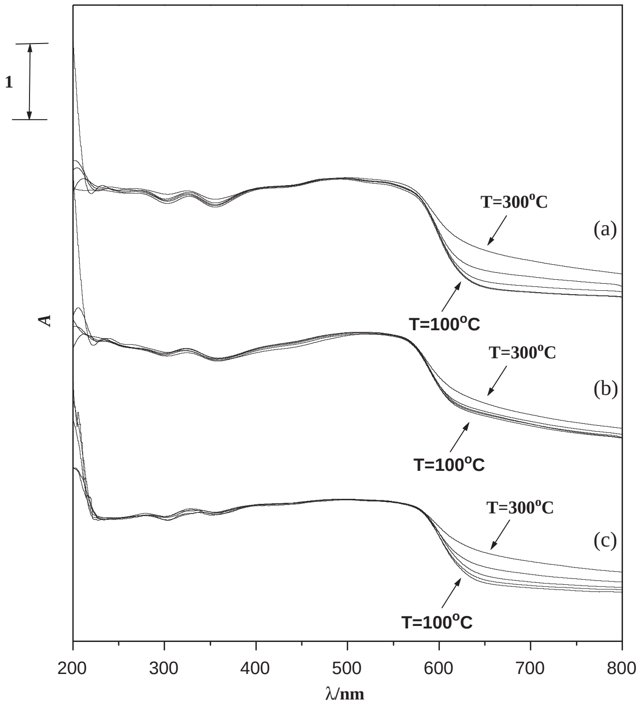

Fig. 6. Diffuse reflectance UV-visible spectra of: (a) C.I. Pigment Red 48:2, (b) C.I. Pigment Red 48:2 anion-pillared LDH and (c) a mixture of after C.I. Pigment Red 48:2 and Mg/Al–NO_3 LDH after thermal aging at different temperatures. Intercalation of the pigment in the LDH host leads to a marked increase in thermostability.

Samples of C.I. Pigment Red 48:2 and C.I. Pigment Red 48:2 anion-pillared LDH were irradiated with a UV-visible source for 20, 40, 60, 80 and 100 min. The color difference (ΔE) values of the resulting materials determined using the CIE 1976 $L^*a^*b^*$ method [18] are shown in Fig. 7. The ΔE values of the pristine pigment are considerably larger than those of the intercalated pigment after irradiation for the same times and the difference increases with time, particularly after 80 min, indicating that the photostability of the pigment is markedly enhanced by intercalation in the layered host. It is generally accepted [23] that the photooxidation of azo dyes involves attack by photochemically generated singlet oxygen and that the hydrazone tautomer is more readily attacked than the azo form. For related azo dyes in solution, it has been shown [22] that the presence of intramolecular hydrogen bonding can protect the

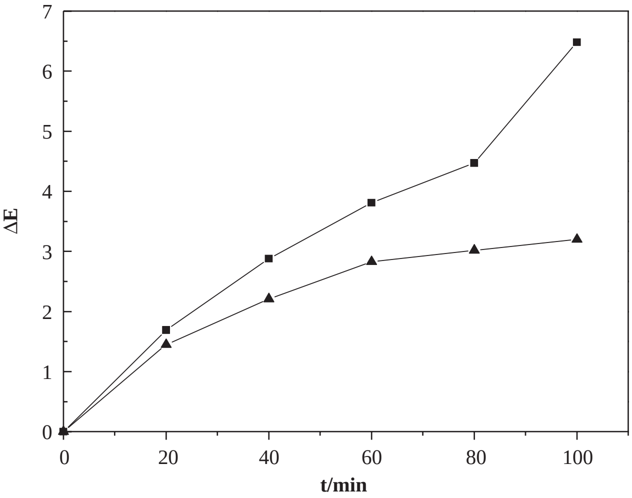

Fig. 7. CIE 1976 $L^*a^*b^*$ color difference (ΔE) values of C.I. Pigment Red 48:2 (■) and C.I. Pigment Red 48:2 anion-pillared LDH (▲) after UV aging for different periods. Intercalation of the pigment in the LDH host leads to a marked increase in photostability.

chromophore from attack by $^1O_2$. This type of intramolecular hydrogen bonding is present in the structure we propose for the intercalated pigment (Fig. 5), suggesting a possible explanation of the enhanced photostability observed on intercalation. Furthermore, as noted above, the quantum chemical calculations suggest that the pigment exists in the interlayer galleries as the azo tautomer, which is expected to more stable to photochemical oxidation than the hydrazone form found in the pristine pigment. For the case of a perylene bisimidetetrasulfonate pigment, where there is no azo chromophore, it was found that the photostability of pristine and LDH-intercalated pigments were very similar [11]. This suggests that the enhanced photostability of C.I. Pigment Red 48:2 compared with the pristine pigment is not merely due to the physical barrier associated with intercalation between the layers and that other factors, such as those proposed above, are indeed involved.

The photostability of the pristine and the intercalated pigments incorporated (0.2 wt%) in polypropylene was also compared. The resulting composites were irradiated with a UV-visible source for 20, 40, 60 and 80 min. The measured color difference values (ΔE) of the resulting materials are shown in Fig. 8. The ΔE values of the composite with the pristine pigment are considerably larger than those of the intercalated pigment after irradiation for the same times, indicating that the enhanced photostability of the intercalated pigment is retained after formation of the polymer composite.

4. Conclusions

A large anionic pigment has been intercalated into a LDH host by ion-exchange of an LDH nitrate precursor with a solution of the calcium salt of the pigment, C.I. Pigment Red 48:2, in ethane-1,2-diol. After intercalation of the pigment, the interlayer distance increases to 1.72 nm. There are complex supramolecular interactions between the host layers and guest anions in the intercalated structure. The pigment-intercalated LDH shows much better photostability under UV irradiation and thermostability than the pristine pigment. When the pigment and pigment-intercalated LDH were separately incorporated in polypropylene composites, the thermo- and photostability of the composite containing the intercalated pigment were also higher than that of the pigment composite.

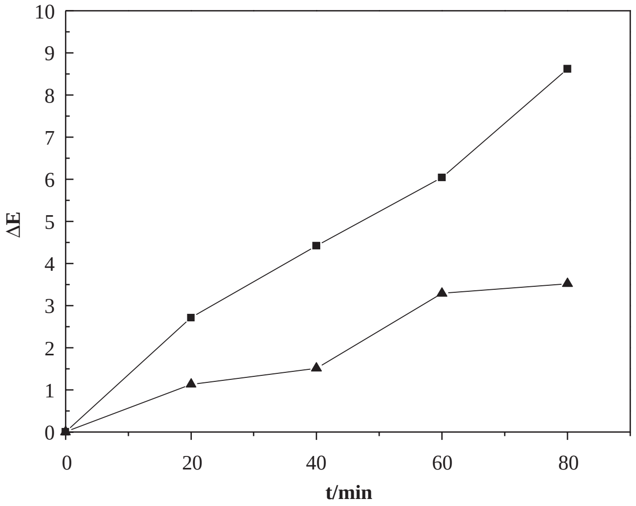

Fig. 8. CIE 1976 $L^*a^*b^*$ color difference (ΔE) values of C.I. Pigment Red 48:2 (■) and C.I. Pigment Red 48:2 anion-pillared LDH (▲) samples incorporated in polypropylene after UV aging for different periods. Intercalation of the pigment in the LDH host leads to a marked increase in photostability of the resulting composite.

Acknowledgments

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References

[1] G. Buxbaum (Ed.), Industrial Inorganic Pigments, 2nd ed, VCH, Weinheim, 1998.
[2] W. Herbst, K. Hunger, Industrial Organic Pigments, 2nd ed, VCH, Weinheim, 1997.
[3] G. Schulz-Ekloff, D. Wőhrle, D. Van Duffel, R.A. Schoonheydt, Micropor. Mesopor. Mater. 51 (2002) 91.
[4] M. Ogawa, K. Kuroda, Chem. Rev. 95 (1995) 399.
[5] R. Hoppe, G. Alberti, U. Costantino, C. Dionigi, G. Schulz-Ekloff, R. Vivani, Langmuir 13 (1997) 7252.

[6] K. Zlatanova, P. Markovsky, I. Spassova, G. Danev, Opt. Mater. 5 (1996) 279.

[7] V. Rives (Ed.), Layered Double Hydroxides: Present and Future, Nova Science Publishers, New York, 2001.

[8] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173.

[9] F. Trifiro, A. Vaccari, Comprehensive supramolecular chemistry, in: J.L. Atwood, D.D. MacNicol, J.E.D. Davies, F.V. Vőgtle, G. Alberti, T. Bein (Eds.), Solid-State Supramolecular Chemistry, vol. 7, Pergamon Press, Oxford, 1996 (Chapter 8).

[10] (a) Y. Park, K. Kuroda, C. Kato, J. Chem. Soc., Dalton Trans. (1990) 3071;
(b) W. Jung, Y. Huh, Bull. Korean Chem. Soc. 17 (1996) 547;
(c) U. Costantino, N. Coletti, M. Nocchetti, G.G. Aloisi, F. Elisei, Langmuir 15 (1999) 4454;
(d) M.Z. Bin Hussein, Z. Zainal, A.H. Yahaya, A. Binti A. Aziz, Mater. Sci. Eng. B 88 (2002) 98.

[11] J. Bauer, P. Behrens, M. Speckbacher, H. Langhals, Adv. Funct. Mater. 13 (2003) 241.

[12] Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., vol. 27, Wiley-VCH, Weinheim, 2002, p. 1.

[13] Y. Zhao, F. Li, R. Zhang, D.G. Evans, X. Duan, Chem. Mater. 14 (2002) 4286.

[14] R. Mausfeld, D. Heyer (Eds.), Colour Perception—Mind and the Physical World, Oxford University Press, London, 2003.

[15] M. Stokes, M.D. Fairchild, R.S. Berns, ACM Trans. Graphics 11 (1992) 406.

[16] M.J. Frisch, et al., Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003.

[17] Z.P. Xu, H.C. Zeng, Chem. Mater. 13 (2001) 4564.

[18] A.R. Kennedy, C. McNair, W.E. Smith, G. Chisholm, S.J. Teat, Angew. Chem. Int. Ed. 39 (2000) 638;
A.R. Kennedy, C. McNair, W.E. Smith, G. Chisholm, S.J. Teat, Angew. Chem. 112 (2000) 652.

[19] J.T. Kloprogge, L. Hickey, J.L. Frost, Appl. Clay Sci. 18 (2001) 37.

[20] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.

[21] (a) P. Desai, E. Couthino, J. Mol. Struct. (Theochem), 528 (2000) 29;
(b) S. Tauro, E. Couthino, J. Mol. Struct. 532 (2000) 23.

[22] H. Zhan, H. Tian, Dyes Pigments 37 (1998) 231.

[23] P. Aranyosi, Z. Csepregi, I. Rusznák, L. Töke, A. Víg, Dyes Pigments 37 (1998) 33.