INTERCALATION OF TARTRAZINE INTO ZnAl AND MgAl LAYERED DOUBLE HYDROXIDES

Ludvík BENEŠ[1,*], Klára MELÁNOVÁ[2], Vítězslav ZIMA[3] and Jan SVOBODA[4]
Joint Laboratory of Solid State Chemistry of the Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic and University of Pardubice,
Studentská 84, 532 10 Pardubice, Czech Republic; e-mail: [1] ludvik.benes@upce.cz,
[2] klara.melanova@upce.cz, [3] vitezslav.zima@upce.cz, [4] jan.svoboda@upce.cz

Received June 15, 2004
Accepted October 13, 2004

The intercalates of Tartrazine Acid Yellow were prepared by heating $[Zn_{0.67}Al_{0.33}(OH)_2]$-$(CO_3)_{0.165}\cdot0.5H_2O$ or $[Mg_{0.70}Al_{0.30}(OH)_2](CO_3)_{0.15}\cdot0.5H_2O$ with a solution of an acid form of Tartrazine in an open reaction vessel or by stirring the powdered calcined hydrotalcites with a Tartrazine solution at room temperature. The intercalates were characterized by chemical and thermal analysis, X-ray powder diffraction and UV-VIS spectroscopy. The intercalates prepared by stirring the calcined host powders have worse crystallinity than those prepared by ion exchange. A possible arrangement of the Tartrazine anions in the intercalates was suggested on the basis of their chemical compositions and interlayer distances, taking into account van der Waals dimensions of the guest anions and assuming that the structure of the host layers is not changed during the intercalation process.

Keywords: Hydrotalcite-like compounds; Hydrotalcites; Intercalations; Intercalates; Dyes; X-ray powder diffraction; Zinc; Aluminium; Magnesium; ZnAl-CO_3; MgAl-CO_3; Solid-state chemistry.

Hydrotalcite-like compounds (HTlcs) or layered double hydroxides (LDHs) are host materials that are of interest because of their potential applications as catalysts, sorbents, hosts for nanoscale reactions as well as in medicine as antacids[1–5]. In general, HTlcs may be represented by the general formula $[M^{II}_{(1-x)}M^{III}_x(OH)_2][x/nA^{n-}]\cdot mH_2O$, where M^{II} (typically Mg, Zn, Ni, or Co) and M^{III} (Al, Cr, or Fe) are divalent and trivalent cations, respectively, and A^{n-} are exchangeable anions of charge n which compensate the positive charge due to the presence of M^{III} in the layers. The anions are accommodated in the interlayer region, where water molecules are also located. Therefore, functional organic or organometallic species with anionic groups (carboxylate, phosphonate, sulfonate) can be intercalated in this class of layered hosts.

Three main methods for the preparation of intercalates with relatively large organic guests have been reported. The first one is a conventional an-

doi:10.1135/cccc20050259

ion exchange[6–9]. Using the most common HTlcs with carbonate anions in the interlayer space as a starting compound has a drawback in that the carbonate anions are strongly held in the interlayer region and it is difficult to replace them with other counter-anions[10]. So HTlcs containing chloride or perchlorate anions are usually used in the exchange reactions. Secondly, organic cations may be incorporated directly by coprecipitation[1,11,12]. The third method is based on the fact that M^{II}–M^{III} mixed oxides, obtained by calcination of a HTlc at about 500 °C, adsorb anions from their aqueous solutions during the reconstruction of the original HTlc structure (memory effect)[4,13–16].

In this paper, intercalates of Tartrazine Acid Yellow ($C_{16}H_9N_4O_9S_2Na_3$) with $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}\cdot 0.5H_2O$ and $[Mg_{0.70}Al_{0.30}(OH)_2](CO_3)_{0.15}\cdot 0.5H_2O$ prepared by ion exchange and by the reconstruction from mixed oxides are described. The structural formula of the Tartrazine anion is given in Fig. 1.

EXPERIMENTAL

Large amounts of ZnAl-CO_3, of the formula $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}\cdot 0.5H_2O$, and MgAl-$CO_3$, of the formula $[Mg_{0.70}Al_{0.30}(OH)_2](CO_3)_{0.15}\cdot 0.5H_2O$, were prepared by the urea method[15]. Solutions obtained by mixing 100 ml of 0.5 M $AlCl_3$, 200 ml of 0.5 M $ZnCl_2$ or $MgCl_2$ and 30 g of urea were refluxed for 2 days. The precipitates obtained were filtered off, washed with distilled water and equilibrated with 100 ml of 0.1 M Na_2CO_3 for one day. Then the solids were recovered, washed with distilled water and dried in air.

The intercalates prepared by the ion-exchange method (designated ZnAl or MgAl) were synthesized by adding 1.23 g of ZnAl-CO_3 or 1.03 g of MgAl-CO_3 (4 mmol) to an aqueous solution of an acid form of Tartrazine. This form was prepared by stirring an aqueous solution of its sodium salt (1.4 g) with ion-exchange resin Amberlite IR 120. The reaction mixtures were heated at 90 °C with stirring in an open vessel for 48 h. The volume of the reaction mixture (400 ml) was kept constant by automatic addition of distilled water[16]. For the preparation of the intercalates using the memory effect (designated ZnAl-mem or MgAl-mem), the host compounds were calcined in air at 500 °C for 3 h. The calcined powders were added to a solution containing 1.4 g of sodium salt of Tatrazine in 200 ml of CO_2-free water

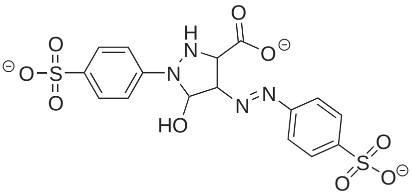

FIG. 1
Structural formula of the Tartrazine anion

and stirred at room temperature for 3 days. All the intercalates prepared were filtered, washed with CO_2-free distilled water and dried in air at room temperature. An excess of Tartrazine was removed from the surface by extraction with ethanol. After extraction, samples were kept in a desiccator containing a saturated solution of NaCl to achieve 76% relative humidity (RH).

The contents of zinc, magnesium, aluminium, and sulfur were determined by an energy-dispersive X-ray spectrometry (EDX) microanalysis. The content of Tartrazine anion was determined by elemental analysis (C, H, N, S) and the water content by thermogravimetry. Elemental analysis: for $[Zn_{0.67}Al_{0.33}(OH)_2](C_{16}H_9N_4O_9S_2)_{0.11}\cdot 1.5H_2O$ (165.0) calculated: 12.82% C, 3.66% H, 3.74% N, 4.28% S; found: 12.96% C, 3.51% H, 3.90% N, 4.05% S for ZnAl; 12.77% C, 3.71% H, 3.66% N, 4.25% S for ZnAl-mem. For $[Mg_{0.70}Al_{0.30}(OH)_2]$-$(C_{16}H_9N_4O_9S_2)_{0.10}\cdot 1.5H_2O$ (132.7) calculated: 14.48% C, 4.48% H, 4.22% N, 4.83% S; found: 14.23% C, 4.67% H, 4.15% N, 4.92% S for MgAl; 14.56% C, 4.70% H, 4.31% N, 4.69% S for MgAl-mem.

Samples with Tartrazine adsorbed on surface were prepared by stirring ZnAl-CO_3 or MgAl-CO_3 with a solution of Tartrazine (sodium salt) at room temperature overnight. The samples prepared were filtered off, washed with a small amount of distilled water and dried.

Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using CuKα radiation with secondary graphite monochromator. Diffraction angles were measured at 2–70° (2θ). In situ temperature XRD measurements were carried out in an MRI chamber at 30–320 °C. Diffraction angles were measured at 2–25° (2θ). TG analyses were performed using a Derivatograph C (MOM Budapest, Hungary). The measurements were carried out in air between 20 and 900 °C at a heating rate of 5 K min^{-1}. UV-VIS absorption spectra (330–1100 nm) were measured using a Perkin–Elmer Lambda 12 spectrometer in a Nujol suspension containing 15% (w/w) of sample.

RESULTS AND DISCUSSION

Carbonate ions are strongly held in the interlayer region of ZnAl-CO_3 or MgAl-CO_3 and cannot be replaced by other anions in neutral or basic medium. This means that Tartrazine cannot be intercalated into ZnAl-CO_3 or MgAl-CO_3 using its sodium salt. Therefore the single-phase products were prepared by heating ZnAl-CO_3 or MgAl-CO_3 with a solution of an acid form of Tartrazine in an open reaction vessel. Heating supports removal of the carbonate anions from solution and thus favors the formation of the products. Virtually the same products were obtained by stirring calcined ZnAl-CO_3 or MgAl-CO_3 suspended in a Tartrazine sodium salt solution.

Figure 2 shows X-ray diffractograms of the intercalates prepared. A series of sharp intensive (00*l*) diffraction lines is observed in the diffractograms together with a (110) line and other (*hkl*) lines with a low intensity. All diffraction lines can be indexed in a hexagonal lattice with lattice parameters given in Table I. Linewidths of the (00*l*) reflections of the intercalates prepared using the memory effect are distinctly greater than those of the intercalates prepared by the ion exchange, i.e., the samples prepared using the memory effect have worse developed crystallites. Similarly to the parent hosts, the ZnAl and ZnAl-mem intercalates have better crystallinity than the corresponding MgAl and MgAl-mem intercalates.

Basal spacings of the intercalates prepared depend on relative humidity. As an example, the diffractograms of ZnAl intercalate are given in Fig. 3. A part of co-intercalated water molecules is released at relative humidity lower than 58% and the crystallinity of the intercalate is worsened. This indicates that the part of water molecules is held in the compound very loosely. It is released also by heating the sample to 60 °C with its (00*l*) diffraction lines becoming significantly broadened. Most probably, both dehy-

TABLE I
Lattice parameters of intercalates of ZnAl or MgAl LDHs and Tartrazine

Sample	*a*, nm	*c*, nm
ZnAl	0.3071(1)	7.139(1)
ZnAl-mem	0.3071(1)	7.141(1)
MgAl	0.3037(4)	7.154(4)
MgAl-mem	0.3034(4)	7.141(3)

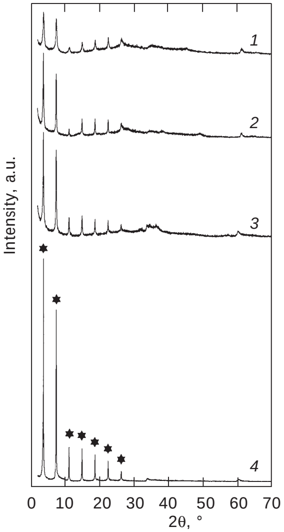

FIG. 2
X-ray diffractograms of MgAl-mem (*1*), MgAl (*2*), ZnAl-mem (*3*), ZnAl (*4*) intercalates. The (00*l*) reflections are marked with an asterisk

drated samples are identical as the diffraction pattern measured at 60 °C is very similar to that of the sample kept at 33% RH at room temperature. By heating above 100 °C, the intercalate becomes almost amorphous. The dehydration is reversible as the samples regained their original basal spacing when kept at a relative humidity of 76%.

Thermogravimetric curves of the ZnAl intercalates together with that of the parent host are shown in Fig. 4. ZnAl-CO_3 decomposes in one step so that it is not possible to distinguish the weight losses caused by the release

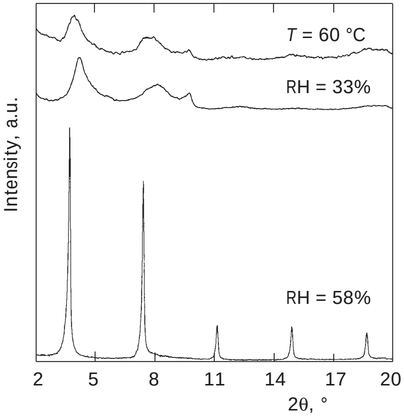

FIG. 3
Diffractograms of ZnAl intercalate measured under different conditions

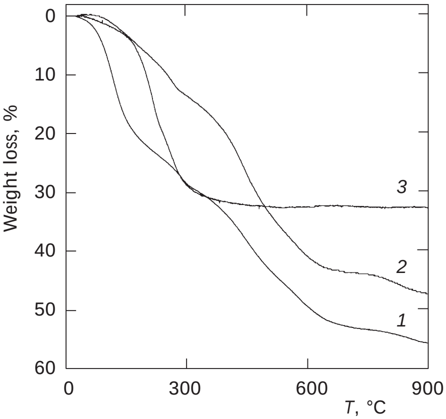

FIG. 4
Thermogravimetric curves of ZnAl intercalate stored at 76% RH (*1*), ZnAl intercalate stored over P_2O_5 (*2*), and pure $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}\cdot0.5H_2O$ (*3*)

of interlayer water, CO_2 from carbonate anions, and the water from dehydroxylation of HTlc. The intercalate stored at 76% RH decomposes in three poorly resolved steps. Interlayer water is released in the first step up to 150 °C and the dehydroxylation occurs between 150–290 °C. The observed weight losses 18 and 10% are in good agreement with the values 16.4 and 10.9% calculated for the sample containing 1.5 H_2O per formula unit. The decomposition of the intercalated Tartrazine occurs in the third slow step above 300 °C. Total weight loss (55.9%) is in good agreement with the value 56.7% calculated for $Zn_{0.67}Al_{0.33}(OH)_2(C_{16}H_9N_4O_9S_2)_{0.11}\cdot 1.5H_2O$. The sample stored over P_2O_5 in vacuum did not contain interlayer water. It decomposes in two steps, the first one (13%) corresponds to dehydroxylation, the other corresponds to thermal decomposition of intercalated Tartrazine. Total weight loss (47.7%) is in good agreement with the value 48.3% calculated for $Zn_{0.67}Al_{0.33}(OH)_2(C_{16}H_9N_4O_9S_2)_{0.11}$.

Thermogravimetric curves of the MgAl intercalates together with that of the parent host are given in Fig. 5. MgAl-CO_3 decomposes in two steps. The intercalate stored at 76% RH decomposes in two poorly resolved steps. The first corresponds to loss of interlayer water and water from dehydroxylation of HTlc. The observed weight loss 33% is in good agreement with the value 33.9% calculated for the sample containing 1.5 H_2O per formula unit. The decomposition of the intercalated Tartrazine occurs in the second slow step above 250 °C. Total weight loss (67.5%) is in good agreement with the value 67.1% calculated for $Mg_{0.70}Al_{0.30}(OH)_2(C_{16}H_9N_4O_9S_2)_{0.10}\cdot 1.5H_2O$. The

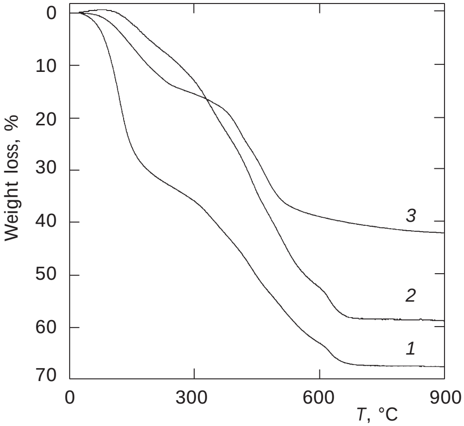

FIG. 5

Thermogravimetric curves of MgAl intercalate stored at 76% RH (*1*), MgAl intercalate stored over P_2O_5 (*2*), and pure $[Mg_{0.70}Al_{0.30}(OH)_2](CO_3)_{0.15}\cdot 0.5H_2O$ (*3*) sample stored over P_2O_5 in vacuum does not contain interlayer water. It decomposes in one step so that it is not possible to distinguish weight losses caused by dehydroxylation of HTlc and by decomposition of intercalated Tartrazine. Total weight loss (58%) is in good agreement with the value 58.8% calculated for $Mg_{0.70}Al_{0.30}(OH)_2(C_{16}H_9N_4O_9S_2)_{0.10}$.

As follows from the composition of the intercalates, Tartrazine must be present as a trianion in the interlayer space, i.e., the positive charge of the layers is compensated not only by both SO_3^- groups but also by the COO^- group. A possible arrangement of the Tartrazine anions in the intercalates was suggested on the basis of their chemical compositions and interlayer distances, taking into account van der Waals dimensions of the guest molecules and assuming that the structure of the host layers is not changed during the intercalation process. The geometry of the Tartrazine anion was optimized using a Hyperchem program. The van der Waals length of the Tartrazine anion l is 2.06 nm and its cross-section area A is estimated to be roughly 1.8 nm^2. Taking into account the tetrahedral geometry of the terminal SO_3^- group, the oxygen atoms of which presumably lie on the surface of the layer in a plane parallel to the plane of the host layers, one S–C bond of Tartrazine could be almost perpendicular to the layer similarly to Methyl-Orange-intercalated ZnAl-HTlc[7]. As follows from a comparison of the van der Waals length of the anion l and the height of the interlayer space $\Delta d = c/3 - d_l = 1.914$ nm, where $c/3$ is the basal spacing and d_l is the thickness of the host layer (4.46 Å), the Tartrazine anions should be tilted to the host layers. The angle α under which the Tartrazine anions are tilted, is $\alpha = \sin^{-1} (\Delta d/l) = 68.3°$. The probable arrangement of the Tartrazine anions is shown in Fig. 6. The Tartrazine anions form a monolayer in the interlayer space of the intercalate. An “equivalent area” surrounding each positive charge in the brucite-like sheet is $3a^2 \sin 60° = 0.25$ nm^2 (lit.[7]). The cross-section area A' of the Tartrazine anion projected onto the plane of the host layer, estimated from the relation $A' = A \cos \alpha$, is less than 0.67 nm^2. As every Tartrazine anion compensates three positive charges of the host layer, the projected cross-section area A' is smaller than the area available for this anion on the layer ($3 \times 0.25 = 0.75$ nm^2). This leads to formation of relatively large cavities among the Tartrazine anions, where co-intercalated water molecules are placed. These water molecules can be easily released which is in agreement with the observed behavior of the intercalates at low relative humidities.

Absorption spectra of the ZnAl and MgAl intercalates, Tartrazine in aqueous solution, and Tartrazine adsorbed on ZnAl-CO_3 are shown in Fig. 7. The spectrum of the Tartrazine solution shows a maximum at 399 nm. The maximum of absorbance of surface-adsorbed Tartrazine is shifted to lower wavelengths (358 nm). In the ZnAl intercalate, the absorption band is broadened and its maximum is shifted to higher wavelengths (439–507 nm). For the MgAl intercalate, the absorption band is very broad (392–515 nm).

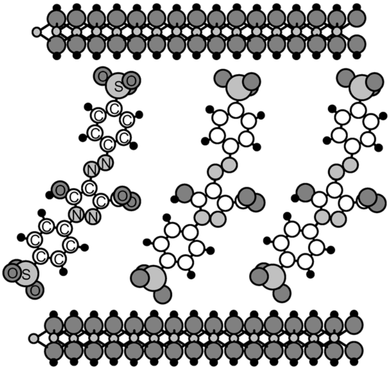

FIG. 6
Possible arrangement of Tartrazine anions in the interlayer space of the intercalates

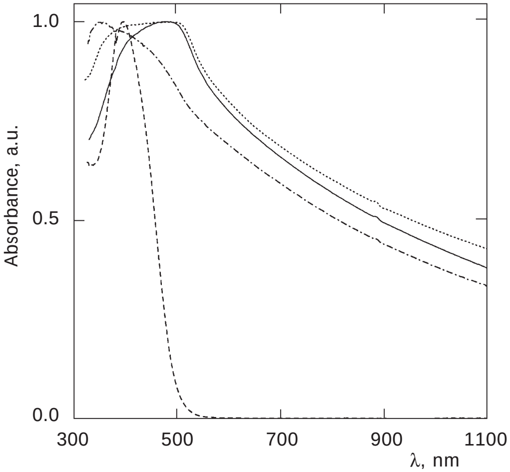

FIG. 7
Normalized absorption spectra of ZnAl intercalate (——), MgAl intercalate (······), an aqueous solution of Tartrazine at pH 7 (------) and Tartrazine adsorbed on ZnAl-CO_3 (-·-·-·)

CONCLUSION

The stirring of solid layered double hydroxides with a solution of an acid form of Tartrazine Yellow provides materials with better crystallinity than the preparation using the memory effect. From the interlayer distances and the amount of the guest anions in the intercalates, the most probable arrangement of the guest molecules in the interlayer space of the host can be deduced. The Tartrazine Yellow molecules are anchored to the host layers with their SO_3^- groups forming a pillared structure. The UV-VIS band of the intercalated dye is significantly broadened compared to this band observed in the spectrum of the dye in the aqueous solution. Also, a bathochromic shift of this band is observed, especially for ZnAl. The intercalates prepared belong among materials which are recently largely studied due to their potential use in photochemical and photophysical devices or as new inorgano-organic pigments.

This study was supported by the Ministry of Education, Youth and Sports of the Czech Republic (MSM253 100001) and by the Academy of Sciences of the Czech Republic (AVOZ 4050913).

REFERENCES

1. de Roy A., Forano C., El Malki K., Besse J.-P. in: *Anionic Clays: Trends in Pillaring Chemistry, Synthesis of Microporous Materials* (M. L. Ocelli and E. R. Robson, Eds), Vol. 2, p. 108. Van Nostrand Reinhold, New York 1992.
2. Cavani F., Trifiro F., Vaccari A.: *Catal. Today* **1991**, *11*, 173.
3. Newman S. P., Jones W.: *New J. Chem.* **1998**, *22*, 105.
4. Trifiro F. Vaccari A. in: *Comprehensive Supramolecular Chemistry* (G. Alberti and T. Bein, Eds), Vol. 7, Chap. 8. Pergamon, Elsevier Science, Oxford 1996.
5. Costantino U., Nocchetti M. in: *Layered Double Hydroxides: Present and Future* (V. Rives, Ed.), Chap. 12. Nova Science Publ., New York 2001.
6. Meyn M., Beneke K., Lagaly G.: *Inorg. Chem.* **1990**, *29*, 5201.
7. Costantino U., Coletti N., Nocchetti M., Aloisi G. G., Elisei F.: *Langmuir* **1999**, *15*, 4454.
8. Miyata S.: *Clays Clay Miner.* **1983**, *31*, 305.
9. Costantino U., Coletti N., Nocchetti M., Aloisi G. G., Elisei F., Latterini L.: *Langmuir* **2000**, *16*, 10351.
10. Rives V., Ullibari M. A.: *Coord. Chem. Rev.* **1999**, *181*, 61.
11. Clearfield A., Kieke M., Kwan J., Colon J. L., Wang R.-C.: *J. Inclusion Phenom.* **1991**, *11*, 361.
12. Kanezaki E., Sugiyama S., Ischikawa Y.: *J. Mater. Chem.* **1995**, *5*, 1969.
13. Chibwe K., Jones W.: *J. Chem. Soc., Chem. Commun.* **1989**, 926.
14. Kanezaki E.: *J. Mater. Sci.* **1995**, *30*, 4926.
15. Kaneyoshi M., Jones W.: *J. Mater. Chem.* **1999**, *9*, 805.
16. Aloisi G. G., Costantino U., Elisei F., Latterini L., Natali C., Nocchetti M.: *J. Mater. Chem.* **2002**, *12*, 3316.

17. Costantino U., Marmottini F., Nocchetti M., Vivani R.: *Eur. J. Inorg. Chem.* **1998**, 1439.
18. Melánová K., Beneš L., Zima V., Vlček M.: *Sci. Pap. Univ. Pardubice, Ser. A* **2002**, *8*, 103.