Structural changes in phenol-intercalated hydrotalcite caused by heating

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ABSTRACT: Thermal analysis (DTA-TG-DTG), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, nitrogen adsorption and mercury intrusion porosimetry techniques were used to assess the structural changes induced upon heating of two hydrotalcite-phenol (trichloro- and trinitrophenol, HT-TCP and HT-TNP) complexes, and the results were compared with those obtained for the original hydrotalcite (HT) sample. The DTA revealed thermal effects that depended on the nature of the interlayer ion in the complexes. The total weight loss (TG-DTA) increased from 37% for the original HT to 40% for HT-TCP and 77% HT-TNP, as the amount of phenol increased. The XRD and FTIR spectroscopy showed that the calcination product (550°C) of the HT-phenol complexes was indistinguishable from that formed from the original HT. Since HT-phenol complexes were prepared by phenol adsorption on calcined HT, our results confirm the recyclability of HT-like compounds as sorbents for phenols.

KEYWORDS: Hydrotalcite, interlayered complexes, organic anions, phenols, porosity, specific surface area, thermal analysis.

Hydrotalcites (HTs) or layered double hydroxides (LDH), have been the subject of increasing interest from many points of view: synthesis and preparation, structural studies, sorbents, catalyst supports or precursors, anion exchangers, etc. (Vaccari, 1995). Their lamellar structure, consisting of positively-charged brucite sheets with hydrated anions in the interlayer, can be considered the anti-type of that of natural clays, and provides HTs with sorptive and anionic exchange properties (Meyn *et al.*, 1990; Cavani *et al.*, 1991; Fornasari *et al.*, 1995). The mixed oxide formed by the thermal decomposition of HTs also has applications as a sorbent and a catalyst (Cavani *et al.*, 1991; Fornasari *et al.*, 1995; Ulibarri *et al.*, 1995). Therefore, the thermal decomposition of the

diverse HTs has received much attention (Reichle *et al.*, 1986; Ulibarri *et al.*, 1987, 1990; Rey *et al.*, 1992; Hudson *et al.*, 1995).

The anionic exchange properties of HTs make them attractive sorbents for anionic or acidic contaminants such as phenols, acidic pesticides and anionic detergents (Meyn *et al.*, 1990; Hermosín *et al.*, 1992, 1993, 1996; Ulibarri *et al.*, 1995; Pavlovic *et al.*, 1997; Celis *et al.*, 1999). These compounds can also be sorbed by rehydration of calcined HT and reconstruction of the layered structure, resulting in the advantage of sorbent recyclability (Ulibarri *et al.*, 1995; Hermosín *et al.*, 1996). Thus, the study of the thermal decomposition of HT-contaminant complexes is important not only to assess interaction mechanisms and decomposition steps, but also for developing strategies for sorbent recycling. In this paper, the thermal decomposition of two HT-phenol complexes and its effects on the textural properties are studied and

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the results compared with those obtained for the original HT sample.

MATERIALS AND METHODS

Preparation of hydrotalcite and hydrotalcite-phenolate complexes

Hydrotalcite, $[\text{Mg}_3\text{Al}(\text{OH})_8]_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, was prepared by the co-precipitation method by adding 250 ml of an aqueous solution containing 0.75 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 mol $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to a vigorously stirred solution (500 ml) containing 1.7 mol NaOH and 0.5 mol Na_2CO_3 , then heating at 80°C for 24 h (Reichle, 1986). An aliquot of the HT thus prepared was calcined at 550°C for 3 h to obtain magnesium aluminium oxide, HT550, $[\text{Mg}_3\text{AlO}_4(\text{OH})]$.

The hydrotalcite-trichlorophenol (HT-TCP) complex was prepared by reconstruction of the layered HT structure from HT550, suspending 0.85 g of HT550 in 200 ml of 75 mM 2,4,5-trichlorophenol (TCP) solution, at pH 13. The hydrotalcite-trinitrophenol (HT-TNP) complex was also prepared by the reconstruction method, suspending 0.5 g of HT550 in 1 litre of 40 mM 2,4,6-trinitrophenol (TNP), at pH 11. The amount of phenol in each complex was determined from the change in TCP or TNP solution concentration as measured by UV-VIS spectroscopy, once the pH was adjusted.

Thermal analysis

Thermal analyses were performed using a Setaram TG-DTA 92 apparatus, model 1618, using 15 mg of sample diluted with 35 mg of Al_2O_3 . Differential thermal analyses (DTA) and thermogravimetric analysis (TG-DTG) were performed in air between room temperature and 700°C using a heating rate of 10°C min⁻¹.

X-ray diffraction analysis and FTIR spectroscopy

The XRD patterns of the samples were obtained on oriented samples by depositing the powders on glass slides, wetting with methanol and drying. The patterns were recorded using a Siemens D5000 diffractometer with $\text{Cu-K}\alpha$ radiation and a scan rate of 2°/min, from 2 to 60°2 θ . The FTIR spectra were recorded, from 4000–400 cm⁻¹ with a resolution of

4 cm⁻¹, in a Nicolet-SPC on KBr disks with 1–2% of sample content. Four temperatures were selected at which HT or HT-phenol samples were heated for 1 h, then cooled at room temperature in a desiccator before XRD and FTIR patterns were recorded.

SSA and porosity measurements

Nitrogen adsorption-desorption isotherms were measured in a Carlo Erba Sorptomatic 1900 apparatus (Fisons Instr., Milan) on samples previously outgassed at 80°C and equilibrated under vacuum for 15 h. Specific surface areas (SSA) were calculated by applying the BET method (Brunauer *et al.*, 1938) to N_2 adsorption data carried out at 77 K and relative equilibrium pressure range of 0.05 < P/P_0 < 0.25.

The SSA and pore-size distributions of the samples in the range of pore radii from 3.7 to 4 × 10⁴ nm were also obtained by Hg intrusion porosimetry using a Carlo Erba 2000 mercury depression and intrusion porosimeter (Fisons Instr., Milan). The samples were outgassed at room temperature for 30 min prior to the recording of the Hg intrusion curve. A value for the surface tension of Hg of 0.48 N m⁻¹ and a contact angle with solids of 141.3° were used assuming cylindrical pores in the calculation.

The error of the measurement of the specific surface area by the two methods above ranged between 2 and 10% for high (>20 m²g⁻¹) and low (<20 m²g⁻¹) surface area values.

RESULTS AND DISCUSSION

HT-phenol complexes

The amount of TNP in the HT-TNP complex, obtained by reconstruction from HT550, was 5400 $\mu\text{mol/g}$ indicating that TNP anions are present in ~100% of the anion exchange capacity (AEC) of HT ($\text{AEC}_{\text{HT}} \approx 5800 \mu\text{mol/g}$). In contrast, the amount of TCP in the HT-TCP complex, obtained by reconstruction, was 2400 $\mu\text{mol/g}$, i.e. only 42% of the anion exchange positions of HT should be occupied by TCP anions. Therefore, CO_3^{2-} and/or OH^- anions should also be present in the interlayers of HT-TCP to balance the AEC of HT. The low acidity or ionizability of TCP ($\text{pK}_a \approx 6.9$) makes it difficult for phenolate to compete with OH^- and CO_3^{2-} anions to reconstruct the HT layer structure during rehydration of HT550.

Thermal analysis

The DTA curve of the original HT sample (Fig. 1A) showed the two characteristic endothermic effects of hydrotalcite at $\sim 150^\circ\text{C}$ and 400°C (Miyata, 1980; Reichle *et al.*, 1986; Sato *et al.*, 1986). The TG-DTG curves (Fig. 1B) show a wide endothermic effect at 150°C corresponding to a weight loss of 22% in three steps, which have been attributed to interlayer water loss (Miyata, 1980; Reichle *et al.*, 1986; Sato *et al.*, 1986) with some additional dehydroxylation (Rey *et al.*, 1992). The second endothermic effect at 400°C corresponds to one weight loss of an additional 15%, from 350 to 500°C , due to simultaneous decarbonation and dehydroxylation. In this step the destruction of the layered structure of hydrotalcite and formation of the Al/Mg mixed-oxide structure takes place (Hibino *et al.*, 1995; Hudson *et al.*, 1995).

The DTA curve of HT-TCP (Fig. 1C) showed two endothermic effects at 108 and 238°C corresponding to two consecutive weight losses of 6% each. This first region corresponding to interlayer water shows a decrease of 10% with respect to the original HT. This decrease in interlayer water could be indicative of the presence of some TCP as anions in the interlayer, which, due to its larger size and hydrophobic character, displaces the water associated with carbonate anions. A third endothermic effect at 394°C overlapping with an exothermic peak at 448°C , corresponds with a weight loss of only 28% which should be due to the simultaneous loss of carbonate, TCP and dehydroxylation, besides the oxidative decomposition (exothermic effect) of TCP (Fig. 1D). This second weight loss, much greater than that corresponding to the original HT, seems to confirm the presence of some TCP sharing the interlayer space with CO_3^{2-} . The substitution of each CO_3^{2-} by two TCP would produce an increase in this second weight loss, although that substitution constitutes a very small proportion of the AEC, and TCP at the external surface would also contribute to that weight loss.

The TG-DTA curves for the HT-TNP sample, were different from those obtained for HT-TCP, but similar to those previously reported for an analogous HT-TNP complex (Ulibarri *et al.*, 1990). The DTA curve (Fig. 1E) shows a very wide and scarcely appreciable endothermic effect in the 100°C region. It follows a very sharp and exothermic peak at 373°C and a weak exothermic

effect at 459°C . Those effects correspond to three weight losses of 2, 58 and 17%, respectively, in the TG-DTG curves (Fig. 1F). The presence of TNP, as a unique interlayer anion, excludes water from that region and has almost no appreciable weight loss between 50 and 250°C . On the other hand, the two weight losses above 300°C are much greater than those of the original HT and occur throughout a unique and very exothermic reaction.

XRD

The XRD patterns of the HT-phenol complexes, together with that of the original HT sample, are shown in Fig. 2. The HT-TCP (Fig. 2B, trace a) complex shows identical basal spacing to that of HT (Fig. 2A, trace a) with a 7.8 Å value indicating that CO_3^{2-} and/or OH^- would be the preferred interlayer anions in HT-TCP and TCP could be adsorbed in a molecular form on the external surface. However, some TCP anions could be sharing the interlayer space in a flat position 3.5 Å wide, which would fit the interlayer distance and balance the small size of the OH^- . This fact agrees with thermal analysis above suggesting the presence of some TCP as an anion in the interlayer. The HT-TNP complex (Fig. 2C, trace a) shows a basal spacing at 13.6 Å characteristic of TNP-saturated HT with the interlayer occupied by TNP anions closely packed in an upright position (Ulibarri *et al.*, 1990, 1995).

Based on the changes observed in DTA-TG analysis, three temperatures (150 , 300 and 550°C) were selected at which the samples (HT, HT-TCP and HT-TNP) were heated before recording the XRD patterns, which are shown in Fig. 2. The XRD patterns in Fig. 2A, traces b and c show a decrease in the intensity of the diffraction lines of HT with increasing temperature until the appearance at 550°C of the diffraction lines at 2.08 and 1.47 Å, corresponding to the mixed Mg/Al oxide (Fig. 2A, trace d). Very similar changes were observed in the XRD patterns of the HT-TCP and HT-TNP complexes (Fig. 2B,C). However, the HT-TCP sample heated at 300°C (Fig. 2B, trace c) showed basal reflections better developed than those of HT heated at 300°C (Fig. 2A, trace c), which could also indicate the presence of TCP in the interlayer, delaying the destruction of the layered structure. On the other hand, the HT-TNP sample heated at 300°C (Fig. 2C, trace c) does not display the residual basal diffraction as does HT heated at

FIG. 1. TG-DTA and TG-DTG plots of HT (A-B), HT-TCP (C-D) and HT-TNP (E-F) samples.

Fig. 2. XRD patterns of (A) HT, (B) HT-TCP, and (C) HT-TNP treated at different temperatures (a = room temperature, b = 150°C, c = 300°C and d = 550°C).

300°C (Fig. 2A, trace c) and begins to develop the mixed-oxide diffraction lines earlier. The high thermal reactivity (explosive character) of TNP causes their loss and decomposition in a very short time, as revealed by thermal analysis (Fig. 2E,F). This loss destroys the layer structure and develops the mixed-oxide structure earlier. The most important feature revealed by XRD in Fig. 2 is that the final products of HT (Fig. 2A, trace d), HT-TCP (Fig. 2B, trace d) and HT-TNP (Fig. 2C, trace d) heated at 550°C were identical. Taking into account that HT-TCP and HT-TNP were obtained from the double mixed-oxide HT550, those XRD patterns show possible evidence of recycling.

FTIR spectroscopy

On the FTIR spectra of the original and heated samples (Fig. 3), the wide band between 3700 and 3200 cm^{-1} on the spectrum of pure HT is attributed to the overlapping $\nu_{\text{O-H}}$ modes of free and H-bonded hydroxyl groups and water molecules (Fig. 3A, trace a). The corresponding water-bending mode, $\delta_{\text{O-H}}$, is located at 1630 cm^{-1} . The intensity of both bands decreased upon heating at 300 and 550°C as a result of water loss (Fig. 3A, traces b

and c). The stretching-vibration band of CO_3^{2-} at 1375 cm^{-1} , with a shoulder at 1493 cm^{-1} (Fig. 3A, trace a), splits into two bands at 1534 and 1399 cm^{-1} upon heating at 300°C (Fig. 3A, trace b), as a consequence of symmetry changes in carbonate anions induced by the loss of interlayer water (Rey *et al.*, 1992).

The IR spectrum of HT-TCP (Fig. 3B, trace a) shows bands at 1578 and 1457 cm^{-1} corresponding to the aromatic ring of TCP and another band at 1382 cm^{-1} , overlapping that at 1375 cm^{-1} of carbonate, attributed also to the TCP $\nu_{\text{C-O}}$ stretching vibration (Bellamy, 1975; Hermosin *et al.*, 1993). In the FTIR spectrum of HT-TNP, bands corresponding to $\nu_{\text{C-H arom}}$ (3090 cm^{-1}), $\nu_{\text{C=C arom}}$ (1647 and 1491 cm^{-1}), $\nu_{\text{N=O}}$ (1558 and 1335 cm^{-1}), and $\nu_{\text{C-O}}$ (1281 cm^{-1}) were identified (Bellamy, 1975; Hermosin *et al.*, 1996) demonstrating the presence of adsorbed TNP (Fig. 3C, trace a). The HT-phenol complexes showed the weakness of those phenol bands upon heating at 300°C as well as new bands at ~2925 and 2855 cm^{-1} (Fig. 3B, trace b, and 3C, trace b). In the case of HT-TNP heated at 300°C, an additional band at 2213 cm^{-1} was also identified (Fig. 4C, trace b). These new bands correspond to inter-

FIG. 3. FTIR spectra of (A) HT, (B) HT-TCP, and (C) HT-TNP treated at different temperatures (a = room temperature, b = 300°C and c = 550°C).

mediate products of the thermal decomposition of TCP and TNP. The 2925 and 2855 cm^{-1} bands could correspond to $\nu_{\text{C-H}}$ of alkyl derivatives and the 2213 cm^{-1} band to $\nu_{\text{C-N}}$ of nitril derivatives in the case of TNP. For all HT, HT-TCP and HT-TNP, the FTIR spectrum of the samples heated at 550°C (Fig. 3A, trace c; 3B, trace c; and 3C, trace c) were very similar, showing only the bands corresponding to a small number of residual hydroxyls or water molecules and CO_3^{2-} anions sorbed on the samples. Thus, FTIR spectroscopy, like XRD of the heated samples, confirms the recyclability of HT550.

SSA and porosity

The values of SSA obtained by the two methods used are summarized in Table 1. The TCP and TNP sorption on HT greatly reduced the SSA of the HT sample (Table 1). This behaviour is similar to that observed by different authors who describe organic molecules which act as bridges between clay packets, producing aggregation and greatly reducing the SSA of clays (Onken & Traina, 1997). This suggests the presence of TCP and TNP at the external surface of the corresponding HT samples.

TABLE 1. Specific surface area (SSA) from N_2 adsorption (N_2) and Hg intrusion (Hg) of HT, HT-TCP and HT-TNP samples pre-heated at 25, 150, 300 and 550°C for 2 h.

Sample	SSA (m^2g^{-1})							
	25°C		150°C		300°C		550°C	
	N_2	Hg	N_2	Hg	N_2	Hg	N_2	Hg
HT	34	80	69	71	74	71	199	129
HT-TCP	3	3	2	3	3	5	133	100
HT-TNP	1	2	2	3	31	1	208	81

FIG. 4. Cumulative and relative Hg pore-volume for HT, HT-TCP and HT-TNP heated at 300 and 550°C.

For HT, HT-TCP and HT-TNP, small changes in SSA were observed after increasing the temperature from 25 to 300°C (Table 1). However, a great increase in SSA for the three samples was obtained after heating at 550°C. For HT and HT-TNP the SSA increased to $\sim 200 \text{ m}^2\text{g}^{-1}$, whereas for HT-TCP the SSA increased to $133 \text{ m}^2\text{g}^{-1}$. The SSA values from Hg intrusion were much lower in the case of samples heated at 550°C. Since Hg does not enter in surface pores below $0.005 \mu\text{m}$, the difference (SSA/N_2 and SSA/Hg) should be due to the microporosity developed during the destruction of layered structure. These smallest pores ($<0.005 \mu\text{m}$) correspond to cratering at the particle surface produced by the loss of CO_2 from carbonate and TNP and TCP oxidation, being more abundant in HT and HT/TNP, and also to their amorphization. Figure 4 shows the distribution of pores in the size range measured by Hg intrusion. Differences between samples heated at 300 and 550°C (Fig. 4) indicate the increase and new formation of pores with radius in the range of $0.005\text{--}0.01 \mu\text{m}$ on HT and HT-phenol samples, respectively, upon heating at 550°C. In the case of the HT-TNP complex, a large increase in the pore-volume in the large-size range (pore radii of $1\text{--}10 \mu\text{m}$) was also observed (Fig. 4). These large pores between 1 and $10 \mu\text{m}$ should correspond to intraparticle surface. The very drastic loss of interlayer TNP (Fig. 2E,F) gives rise to the formation of very small particles of the corresponding HT-TNP550, with the largest SSA values and very large intraparticle porosity.

CONCLUSIONS

Thermal analysis (DTA-TG-DTA) of HT and HT-phenolate complexes revealed thermal effects and weight losses that depended on the nature of the interlayer anion (inorganic: CO_3^{2-} or organic: phenolate) and on the homoionic or heteroionic character of the HT-phenolate complexes. The water loss was lower in HT-phenolate complexes than that in pure HT and the organic anions were lost at approximately the same temperature as carbonate, but through exothermic effects. Nitrogen adsorption and Hg porosimetry data showed that the calcination of IIT or HT-phenolate complexes resulted in the formation of pores with very well defined radii of $0.005 \mu\text{m}$, with large porosity at $1\text{--}10 \mu\text{m}$ in the case of IIT-TNP. The resulting Al/Mg mixed-oxides, however, were indistinguishable by XRD or FTIR techniques.

Taking into account that the HT-TCP and HT-TNP products were prepared from calcined HT, our results confirm the 'recyclability' of calcined hydrotalcites as adsorbents for phenols making them very attractive filters to remove this kind of anionic contaminant from water.

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REFERENCES

- Bellamy L.J. (1975) *The Infrared Spectra of Complex Molecules* (Vol. 1, 3rd edition). Chapman & Hall, New York.
- Brunauer S., Emmett P.H. & Teller E. (1938) Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**, 309–319.
- Cavani F., Trifirò F. & Vaccari A. (1991) Hydrotalcite-type anionic clay minerals: preparation, properties and applications. *Catal. Today*, **11**, 173–301.
- Celis R., Koskinen W.C., Cecchi A., Bresnahan G., Carrizosa M.J., Ulibarri M.A., Pavlovic I. & Hermosin M.C. (1999) Sorption of the ionizable pesticide imazamox by organoclays and organohydrotalcites. *J. Environ. Sci. Health*, **B34**, 929–941.
- Formasari G., Gazsano M., Mattensi D., Trifirò F. & Vaccari A. (1995) Structure and reactivity of high surface area Ni/Mg/Al mixed oxides. *Appl. Clay Sci.* **10**, 69–82.
- Hermosin M.C., Ulibarri M.A., Mansour M. & Cornejo J. (1992) Assaying sorbents for 2,4-D from waters. *Fresenius Environ. Bull.* **1**, 472–481.
- Hermosin M.C., Pavlovic I., Ulibarri M.A. & Cornejo J. (1993) Trichlorophenol adsorption on layered double hydroxide: a potential sorbent. *J. Environ. Sci. Health*, **A(28)**, 1875–1888.
- Hermosin M.C., Pavlovic I., Ulibarri M.A. & Cornejo J. (1996) Hydrotalcite as sorbent for trinitrophenol: sorption capacity and mechanism. *Water Res.* **30**, 171–177.
- Hibino T., Yamashita Y., Kosuge K. & Tsunashima T. (1995) Decarbonation behavior of Mg-Al- CO_3 , hydrotalcite-like compounds during heat treatment. *Clays Clay Miner.* **43**, 427–432.

- Hudson M.J., Carlino S. & Apperley D.C. (1995) Thermal conversion of a layered (Mg/Al) double hydroxide to the oxide. *J. Mater. Chem.* **5**, 323–329.
- Meyn M., Beneke K. & Lagaly G. (1990) Anion-exchange reactions of layered double hydroxides. *Inorg. Chem.* **29**, 5201–5207.
- Miyata S. (1980) Physicochemical properties of synthetic hydrotalcites in relation to composition. *Clays Clay Miner.* **28**, 50–56.
- Onken B.M. & Traina S.J. (1997) The sorption of anthracene to humic acid-mineral complexes: effect of fractional organic carbon content. *J. Environ. Qual.* **26**, 126–132.
- Pavlovic I., Ulibarri M.A., Hermosin M.C. & Cornejo J. (1997) Sorption of an anionic surfactant from water by a calcined hydrotalcite-like sorbent. *Fresenius Environ. Bull.* **6**, 266–271.
- Reichle W.T. (1986) Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). *Solid State Ionics*, **22**, 135–141.
- Reichle W.T., Kang S.Y. & Everhardt D.S. (1986) The nature of the thermal decomposition of a catalytically active anionic clay mineral. *J. Catal.* **101**, 352–359.
- Rey F., Fornés V. & Rojo J.M. (1992) Thermal decomposition of hydrotalcites: An infrared and nuclear magnetic resonance spectroscopic study. *Chem. Soc. Faraday Trans.* **88**, 2233–2238.
- Sato T., Kato K., Endo T. & Shimada M. (1986) Preparation and chemical properties of magnesium aluminium oxide solid solutions. *React. Solids*, **2**, 253–260.
- Ulibarri M.A., Hernandez M.J. & Cornejo J. (1987) Changes in textural properties derived from the thermal decomposition of synthetic pyroaurite. *Thermochim. Acta*, **113**, 79–86.
- Ulibarri M.A., Luque J.M. & Cornejo J. (1990) Heating-induced effects on the anionic clay minerals $[\text{Al}_2\text{Li}(\text{OH})_6](\text{picrate}) \cdot n\text{H}_2\text{O}$. *Materials Chem. Phys.* **25**, 81–90.
- Ulibarri M.A., Pavlovic I., Hermosin M.C. & Cornejo J. (1995) Hydrotalcite-like compounds as potential sorbents of phenols from water. *Appl. Clay Sci.* **10**, 131–145.
- Vaccari A. (1995) Introduction to the synthesis and applications of anionic clays. *Appl. Clay Sci.* **10**, 1–3.