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Synthesis and characterization of a novel Mg/In layered double hydroxide

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A new brucite-like Mg/In layered double hydroxide of composition $[Mg_{0.725}In_{0.275}(OH)_2][CO_3]_{0.137}\cdot 0.70H_2O$ has been studied.

Layered double hydroxides (LDHs) are anionic clays in which divalent cations (Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, *etc.*) within brucite-like layers are replaced by trivalent cations (Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, La^{3+}, *etc.*) which are of general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})\cdot m H_2O$, where A^{n-} is an anion (CO_3^{2-}, SO_4^{2-}, NO_3^{-}, PO_4^{3-}, Cl^{-}, *etc.*).[1–3] LDHs are effective adsorbents,[4] chromatographic stationary phases[5] and ion exchangers.[6] Hydrotalcites and hydrotalcite-like compounds belong to this class of materials. Hydrotalcite-derived mixed oxides are used as ion exchangers, catalysts and catalyst supports, because of their high surface area and basic surface properties. Thus, they are receiving much attention lately as they facilitate a variety of organic reactions useful in fine chemistry processes.[7,8]

Although indium belongs to the same group as aluminium (ionic radius = 0.50 Å) and gallium (ionic radius = 0.62 Å), the former possesses a larger atomic volume (ionic radius = 0.81 Å), so its inclusion can distort LDH layers. In any case, the effects of introducing a bulkier, more basic cation than aluminium in an LDH on the structural and catalytic properties of the solid are theoretically quite interesting.

This paper reports the synthesis of a novel Mg/In layered double hydroxide and its characterization by different experimental techniques. The surface properties of the materials obtained from different thermal treatments were also determined.

The Mg/In LDH was obtained by using a coprecipitation method. For this purpose, a solution containing 5.00 g of $In(NO_3)_3\cdot 5H_2O$ (0.01 mol l^{-1}) and 9.84 g of $Mg(NO_3)_2\cdot 6H_2O$ (0.03 mol l^{-1}) in 50 ml of deionized water was slowly dropped over 175 ml of an Na_2CO_3 solution at pH 10 at 333 K, with vigorous stirring. The pH was kept constant by adding appropiate volumes of NaOH (1 mol l^{-1}) during precipitation. The suspension thus obtained was kept at 353 K for 24 h, after which the solid was filtered off, washed with 2 l of deionized water, and dried at 373 K. This solid was named HT-1. Any residual nitrate ions in the LDH structure were removed by exchange with carbonate ions. Thus, 5 g of solid HT-1 were added to a solution of 0.5 g of Na_2CO_3 in 200 ml of deionized water, and the suspension was refluxed for 2 h. The solid, which was filtered off and dried at 373 K, was named HT-2. This solid was calcined at 823 or 1073 K for 6 h.

Solids were characterized by elemental analysis, thermogravimetric analysis (TGA), powder X-ray diffraction (XRD), diffuse reflectance infrared spectroscopy (DRIFT), and N_2 sorptometry.

The elemental analysis of the Mg/In LDH following ion exchange with carbonate gave the following formula for an Mg/In ratio of 2.64: $[Mg_{0.725}In_{0.275}(OH)_2][CO_3]_{0.137}\cdot m H_2O$. XRD patterns (Fig. 1) exhibited a single crystalline phase with the hydrotalcite structure in both its original form (HT-1) and after ion exchange (HT-2).[9,10] The unit cell constant (*a* and *c*) and the lattice distance d_{003} for hydrotalcite structures with hexagonal 3*R* symmetry are shown in Table 1. The value of *c* was decreased by the ion exchange as a result of the increased attraction between brucite-like layers and CO_3^{2-} ions, of greater charge than NO_3^{-} ions. The value of *a* is essentially unaffected by the nature of the anion. A comparison of the values for the lattice parameters with reported values for Mg/Al and Mg/Ga LDHs with a similar Mg/M^{III} ratio reveals that the chief effect of replacing aluminium and gallium with indium in the LDH structure is an increase in the value of *a* as a result of the higher atomic radius of indium. Thus, Mg/Al LDHs with a Mg/Al ratio of 2.5 were found to have an *a* value of 3.046 Å,[11] and a Mg/Ga LDH with a ratio of 2.5 an *a* value of 3.10 Å.[12] The calcination of sample HT-2 at 823 K destroyed the LDH structure and led to the formation of a periclase magnesium oxide phase together with an amorphous background. The solid became more

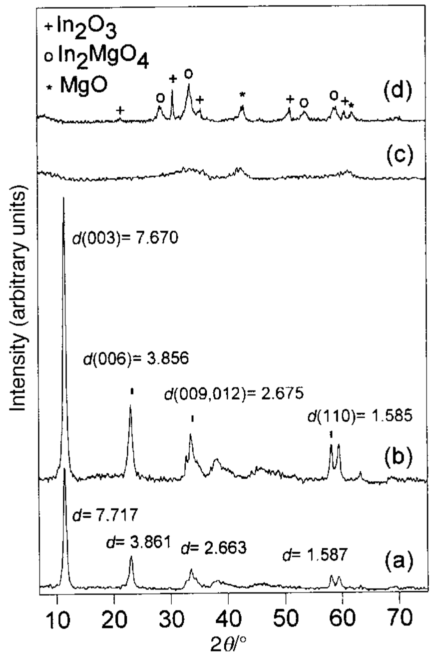

Fig. 1 Powder XRD patterns for solids HT-1 (a), HT-2 (b) and HT-2 calcined at 823 (c) and 1073 K (d).

Table 1 Lattice parameters for synthesized LDHs

Sample	d_{003}/Å	*a*/Å	*c*/Å
HT-1	7.717	3.174	23.15
HT-2	7.670	3.170	23.01

Table 2 Specific surface area (S_{BET}), pore diameter and pore volume of calcined HT-2

T_{calc}/K	S_{BET}/m^2 g^{-1}	Pore volume/ml g^{-1}	BJH pore size/Å
823	60	0.504	262
1073	50	0.471	290

crystalline on calcination at 1073 K, exhibiting bands for MgO and In_2O_3, and others associated with a spinel phase, In_2MgO_4.

The TGA curve for sample HT-2 exhibits two stages spanning the ranges 380–480 and 590–693 K, which involve an overall weight loss of 34.3%. The first such loss (12.3%) can be ascribed to the release of weakly adsorbed interlayer water; the second (22.0%) is associated with the removal of water molecules from the brucite-like structure and of CO_2 from interlayer carbonate as the layered structure is destroyed. Thus, the experimental value for the number of water molecules (m) in the general chemical formula is 0.70.

The DRIFT spectrum for HT-2 includes a strong band between 3800 and 2700 cm^{-1} that comprises among others the twisting vibrations of physisorbed water and vibrations of structural OH groups.The band corresponding to the vibration mode δ_{HOH} appears at 1643 cm^{-1} (ref. 13). A sharp band at 1385 cm^{-1} corresponds to the mode ν_3 of interlayer carbonate and a shoulder at 1049 cm^{-1} to the mode ν_1 for carbonate in the interlayer space.[14] The calcination treatment produces significant changes. Thus, a broad weak band centered at 1400 cm^{-1} is characteristic of O–C–O vibrations in adsorbed carbonate groups on the surface of the oxide system. Another weak band is observed in the 3800–3100 cm^{-1} region. The bands between 450 and 650 cm^{-1} correspond to characteristic vibrations of oxides.[15] Based on these results, the loss of water and CO_2 from these solids upon calcination is quite apparent.

Table 2 gives the specific surface areas (S_{BET}), pore diameters and pore volumes of the hydrotalcite-derived mixed oxides. The surface area decreases with the calcination temperature. The N_2 adsorption–desorption isotherms are of type IV (*i.e.* typical of mesoporous solids) (Fig. 2), the pore size in which varies over wide ranges, with type H1 hysteresis cycles.[16] These solids have smaller surface areas than mixed Mg–Al and Mg–Ga oxides derived from similar hydrotalcites.[8,12]

In summary, our results suggest that Mg/In layered double hydroxides can be synthesized by using a classical coprecipitation procedure. Other experimental variables such as temperature, concentrations, metal sources, anions, *etc.*, can be altered as required in order to obtain materials with different Mg/In ratios and physico-chemical properties. Also, it may be possible to synthesize analogous hydrotalcite-like compounds with other different divalent cations. In_2O_3, In_2O_3–ZnO and Sn-doped In_2O_3 are useful as gas sensors, conductors and catalysts.[17,18] Thus, mixed oxides derived from Mg/In hydrotalcites could find some interesting future applications.

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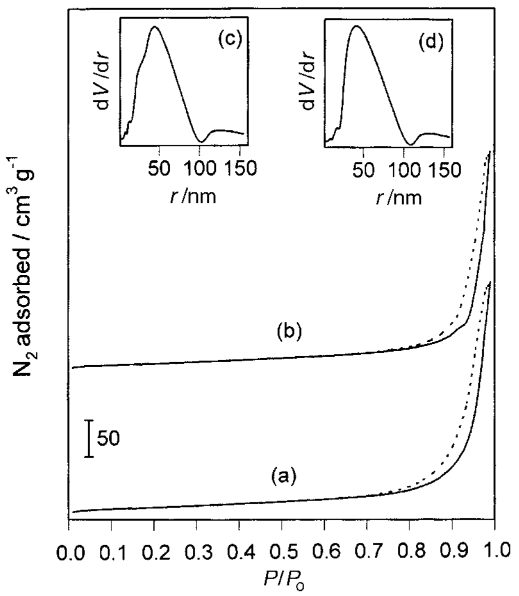

Fig. 2 N_2 adsorption (solid line) and desorption (dotted line) isotherms for solid HT-2 calcined at 823 (a) and 1073 K (b). Insets: BJH pore diameter (r) distribution of solid HT-2 calcined at 823 (c) and 1073 K (d).

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