A New Hydrotalcite-like Compound Containing V^{3+} Ions in the Layers

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Received April 27, 1993

Layered double hydroxides (LDHs) are compounds complementary to clays that contain positively charged layers and anions in the interlammelar space.[1] Their general formula is $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2](Y)_x{\cdot}nH_2O$. Hydrotalcite (HT), $Mg_6Al_2(OH)_6CO_3{\cdot}4H_2O$, has a brucite-like structure, and partial substitution of Al^{3+} for Mg^{2+} (6-fold coordinated by hydroxyl groups) leads to positively charged layers, balanced by interlayer carbonate anions. The preparation, properties, and applications of HT-materials have been reviewed recently.[2] They are used as adsorbents, basic catalysts, catalyst precursors, anionic exchangers, polymer stabilizers, and antacid drugs.

Layered double hydroxides with the hydrotalcite structure containing Al^{3+}, Fe^{3+}, Cr^{3+}, and Sc^{3+} [2] and Co^{3+} [3] have been described, but here we report on a HT-like material containing V^{3+} ions in the layers. It had been claimed[2] that difficulties in synthetizing V^{3+}-containing HTs were due to the instability of this oxidation state for vanadium. Characterization has been carried out by XRD, TG/DTA, and XANES, EXAFS, and FT-IR spectroscopies.

Preparation was performed under a nitrogen atmosphere by using Schlenk techniques.[4] All chemicals were from Fluka, and gases were from Sociedad Espanola del Oxigeno, with adequate purity (better than 99.99%). A 200-mL volume of a 0.5 M VCl_3 and 1 M $MgCl_2{\cdot}6H_2O$ solution was added dropwise to 250 mL of a 0.8 M $Na_2CO_3{\cdot}10H_2O$ and 2.8 M NaOH solution at room temperature. Water had been previously twice distilled and deoxygenated by boiling for 15 min and cooling down to room temperature while continuously bubbling nitrogen. The mixture was magnetically stirred for 2 h at room temperature. Then the volume was reduced to ca. 50%. The suspension was hydrothermally treated at 400 K for 18 days in a stainless steel/Teflon digestion bomb. The gray solid thus obtained was filtered out and washed with deoxygenated water until the absence of Cl^- and Na^+ ions was confirmed in the washing liquids. The solid was finally dried in an oven at 373 K for 8 h.

Chemical analysis for Mg and V was carried out by atomic absorption (ELL-240 Mark-2, Servicio General de Analisis Quimico, Universidad de Salamanca). The carbon content was determined in a 2400 CHN Perkin-Elmer analyzer. Results were as follows: Mg (19.7%), V (16.7%), C (2.0%). Differential thermal analysis (DTA, Perkin-Elmer DTA 1700) showed an intense endothermic peak at 510 K, both in air and in nitrogen. In air it was followed by an intense exothermic peak at 767 K, which was absent in nitrogen and, thus, is ascribed to oxidation of V^{3+} ions. Thermogravimetric analysis (TG, Perkin-Elmer TGS-2) showed a weight loss of 14.9% up to 488 K, where an inflection point appears, both in air and in nitrogen. This low-temperature weight loss in HT-like materials is due to removal of interlayer water molecules.[5] The FT-IR spectrum (Perkin-Elmer FT-IR 1730, KBr pellet technique) showed the presence of carbonate ions, with bands at ν_3 = 1363 cm^{-1}, ν_4 = 671 cm^{-1}; ν_1 and ν_2 were recorded as very weak shoulders at 1053 and 839 cm^{-1}, respectively. Values for hydrotalcite were 1360, 680, 1050, and 865 cm^{-1}, respectively.[6] From chemical analysis and weight loss, the formula of the compound synthetized can be written as $[Mg_{0.71}V_{0.29}(OH)_2](CO_3)_{0.15}{\cdot}0.73H_2O$ (Mg, 19.6%; V, 16.8%; C, 2.0%).

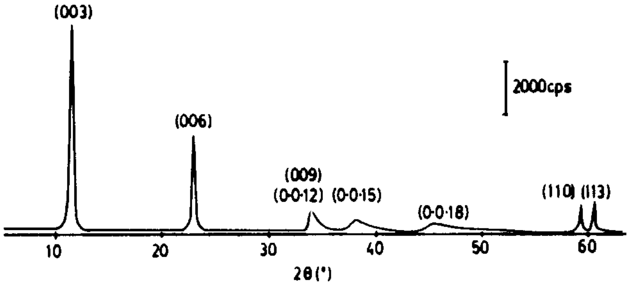

Figure 1. X-ray diffraction diagram of Mg,V–CO_3 double hydroxide.

The X-ray diffraction (XRD) diagram (Siemens D-500, equipped with a Diffract-AT and DACO-MP microprocessor, Ni-filtered, Cu $K\alpha_1$ radiation) is shown in Figure 1. It corresponds to a well-crystallized HT-like material. The indexing of the diffraction peaks was obtained by comparison with the diagram reported for hydrotalcite.[7] The c-axis parameter (22.83, 22.81 Å for hydrotalcite[8]) was calculated from the positions of the (003) and (006) peaks, and the a-axis parameter was 3.10 Å (3.05 Å for hydrotalcite[8]), calculated from the position of the (110) peak ($a = 2d_{(110)}$).

The oxidation state and local coordination of V ions were assessed by X-ray absorption spectroscopy (XAS). Room-temperature vanadium K-edge X-ray absorption spectra were recorded in transmission mode at station XAS-III at the LURE-DCI storage ring (Orsay, France). Monochromatization was achieved with a double silicon crystal working at the (311) reflection. Energies were calibrated using a vanadium metal foil and setting its first peak in the derivative spectrum at 5465 eV. The normalized V K-edge XANES spectrum is shown in Figure 2. It almost coincides with that reported by Wong et al.[9] for roscoelite, a one-layer monoclinic mica in which the Al^{3+} ions in

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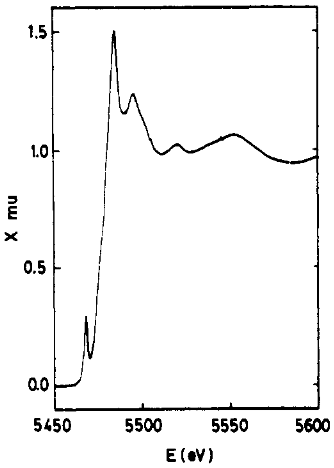

Figure 2. Normalized V K-edge XANES spectrum of Mg,V–CO_3 double hydroxide.

the octahedral [AlO_6] sheet are partially substituted (17%) by V^{3+} ions in distorted octahedra.[10] The low intensity (*ca.* 0.3) of the pre-edge peak at 5468 eV confirms the +3 state of most of the vanadium ions, although the intensity is slightly higher than that reported for roscoelite (*ca.* 0.1). Higher normalized intensities (0.79–1.06) are reported for V^{5+} ions.

Actually, the presence of a very small amount of V^{5+} species could be inferred from the chemical analysis for vanadium and carbon. If all vanadium was present as V^{3+}, the V/C atomic ratio would be 2. Lower values indicate the existence of vanadium species in an oxidation state larger than +3. If we assume that vanadium is only in the +3 and +5 states, the percentage of V^{5+} is only 2% and is probably formed through partial oxidation of V^{3+} cations in the edges or in the external layers of the crystallites.

Best fit analysis of first-shell oscillations in the EXAFS spectrum separated by Fourier transform techniques leads to similar conclusions. The O/V ratio is 6.0, with a V–O distance of 2.04 Å, suggesting an octahedral coordination of V^{3+} cations similar to that found in V_2O_3 (three oxygen atoms at 1.96 Å and other three at 2.06 Å[11]) and roscoelite (six oxygen atoms at ca. 2.0 Å[10]). Simultaneously, a second coordination shell is present and can be associated with vanadium and/or magnesium ions at ca. 3.0 Å within the layers. It should be noted that for the hexagonal-packed layers in brucite, the closest metal–metal distance coincides with the *a* parameter of the crystal, which in this case was 3.10 Å.

We conclude that the material synthesized has a well-crystallized hydrotalcite-like structure with isomorphical substitution of V^{3+} ions for Mg^{2+} ions in octahedral sites.

Acknowledgment. The authors are thankful for the financial support from the CICYT (Grant MAT91-767) and the Junta de Castilla y Leon (Consejeria de Cultura y Turismo). Thanks are also given to Dr. B. Macias for his assistance with chemical analysis.

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