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Direct Synthesis of Polyoxovanadate-Pillared Layered Double Hydroxides

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The use of layered materials for the generation of porous solids with controlled surface properties is now known to be an effective procedure for generating both micro- and mesoporous materials.[1] Layered double hydroxides (LDHs) are an important class of such layered hosts. They have the general formula $[M_{1-x}M'_x(OH)_2][A_{n/x}\ mH_2O]$, where M is a divalent cation and M′ is a trivalent cation, x is equal to the ratio M′/(M + M′) and A is an anion (of charge n) intercalated between the layers.[2] While LDHs themselves have numerous potential applications,[2] the availability of pillared derivatives of LDHs will significantly increase their range of application. In particular the incorporation of polyoxometalate anions of the type $[V_{10}O_{28}]^{6-}$ has been extensively studied.[3-8]

The principal strategy for the preparation of pillared LDHs is based upon conventional anion exchange, with chloride and nitrate anions found to be significantly easier to displace than carbonate.[2] More recently, the exchange of carbonate by $[V_{10}O_{28}]^{6-}$ at pH 4.5 has been reported,[9] although it is thought likely that this reaction goes via an exchange reaction of a chloride intermediate phase. A second method for incorporating polyoxometalates is based on the fact that calcined LDHs have a memory effect, and upon exposure of the oxide to aqueous solutions, they rehydrate and reconstruct the original LDH structure.[10] This route has been used to introduce both organic and inorganic anions between the layers.[11-13] The ease and extent of reconstruction of the intermediate oxide are, however, critically controlled by the properties of the divalent and the trivalent cations forming the sheets as well as the temperature of calcination.[13,14]

Both methods, however, require the reactions to be performed in an inert gas atmosphere because the incorporation of carbonate from atmospheric CO_2 is a dominant side-reaction.

A third approach (the direct synthesis by coprecipitation in the presence of the pillaring anion) has been reported primarily for organic anions,[15] and the production of a truely intercalated layered structure has been found to be dependent upon the value of the layer charge (which may be controlled by the divalent/trivalent cation ratio in the starting salt solutions), the nature of the anion in the starting salt solutions, and the pH of coprecipitation.[16]

Of particular interest is that recently, Narita et al.[17] have reported the direct synthesis of a Zn–Al LDH containing α-$[SiW_{11}O_{39}]^{8-}$. The reaction was performed in an argon atmosphere. We describe here an important extension of this direct synthesis method. In particular we show that a Zn–Cr LDH with $[V_{10}O_{28}]^{6-}$ as the charge-balancing anion may be directly prepared. In addition we also comment upon the effect of the Zn/Cr ratio and the pH of coprecipitation upon the structure of the resulting LDH. We also report on the preparation of Zn–Al LDHs at various pH values.

Experimental Section. A 4 g sample of sodium metavanadate ($NaVO_3$) was dissolved in 100 cm^3 of deionized water, and the pH lowered to 4.5 by adding a solution of 1 M hydrochloric acid. For a Zn/Cr ratio of 2, 2.68 g of anhydrous zinc chloride and 2.62 g of chromium chloride hexahydrate were dissolved in 50 cm^3 of deionized water. This solution was then added to the decavanadate solution, with the pH held constant at 4.5 by the addition of a 1 M sodium hydroxide solution. The mixing was at 55 °C, in an air atmosphere. The slurry was aged overnight at 55 °C. Precipitation was also carried out at different values of the Zn/Cr ratio. Additionally, the influence of the pH of the original vanadate solution and the pH of coprecipitation have been studied. Similar procedures were followed for the Zn–Al system, using anhydrous zinc chloride and aluminum chloride hexahydrate. All the chemical reagents were supplied by Aldrich Chemical Co. Samples were characterized by powder X-ray diffraction (PXRD), FTIR, and thermogravimetric analysis (TGA).[8]

Results and Discussion. Figure 1a presents a PXRD pattern of the material precipitated at pH 4.5 in the presence of the $[V_{10}O_{28}]^{6-}$ anion. (003), (006), and (009) reflections are well defined and correspond to 11.89, 5.90, and 3.90 Å, respectively. This indicates a gallery height close to 7 Å, and suggests the presence of $[V_{10}O_{28}]^{6-}$ anions with an orientation in which the main C_2 axis is parallel to the host layers.[5,6] A broad low intensity peak around 9.8 Å, 10°/2θ; Cu Kα radiation, is present, and this can be related to the formation of an impurity phase most likely consisting of Zn and/or Cr vanadium salts generated during the precipitation.[12,17]

Additional PXRD patterns suggest that an expanded structure with $[V_{10}O_{28}]^{6-}$ is possible for solution ratios of Zn/Cr between 1 and 5. Close examination of the position of the 110 reflection, however, indicates that the lattice **a** parameter value remains relatively constant at 3.11 Å and is independent of the starting Zn/Cr ratios. This suggests that at pH 4.5 there is a preferred Zn/Cr precipitate ratio (close to 2) irrespective of the ratio in the starting solutions. Similar observations have been reported by de Roy et al.[18] with chloride anion and may suggest a preferred ordering of the divalent and trivalent cations within the LDH sheets.

This direct coprecipitation was then repeated at different pH values to explore the possibility of incorporating other vanadate

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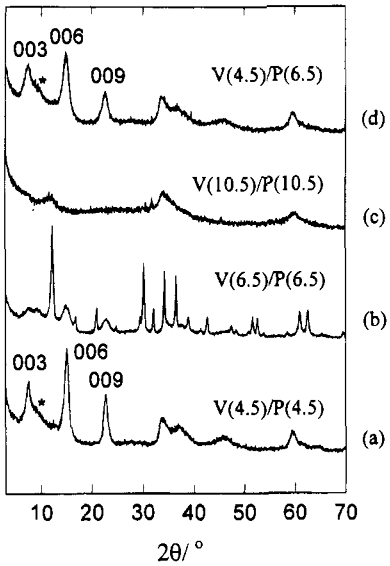

Figure 1. PXRD patterns of Zn−Cr LDH obtained by direct synthesis in metavanadate solution. V(4.5)/P(4.5) indicates that the pH of metavanadate solution is initially adjusted to pH 4.5, and P(4.5) indicates that the precipitation is performed at pH 4.5. Parts a−c involve precipitation at the original pH of the vanadate solution. Part d involves an initial pH of 4.5, adjusted to pH 6.5 prior to precipitation at pH 6.5. An impurity phase which is produced during the synthesis is indicated by an asterisk.

anions.[19] At pH 6.5 a layered structure is not obtained (Figure 1b), only a Zn−Cr and/or metavanadate salt results. In the pH range of 8.5−10.5 (Figure 1c) a disordered LDH structure is obtained (defined by (003), (012) and (110) reflections) with d_{003} around 7.45 Å, and probably corresponds to a chain of metavanadate anions between the layer.[13] Hence under these conditions $[V_{10}O_{28}]^{6-}$ is incorporated only at a precipitation pH of 4.5.

The possible incorporation of $[V_{10}O_{28}]^{6-}$ at a pH other than 4.5 was, therefore, investigated in the following way. A solution of metavanadate was first adjusted to pH 4.5 before changing to pH 6.5, 8.5 or 10. This new pH was then held constant during the addition (and precipitation) of the Zn and Cr solutions. Figure 1d indicates that an expanded LDH structure comparable to that shown in Figure 1a is now obtained at pH 6.5, confirming that the $[V_{10}O_{28}]^{6-}$ generated at pH 4.5 is sufficiently stable to be intercalated at higher values of pH. This expanded structure is not produced, however, at pH 8.5. Instead a zinc−chromium and/or metavanadate salt is precipitated. At high pH values close to 10.5, a fairly disordered LDH structure is formed with, as expected, a metavanadate species rather than $[V_{10}O_{28}]^{6-}$ incorporated. The results indicate that the $[V_{10}O_{28}]^{6-}$ species are sufficiently stable at pH 6.5 to be intercalated.

The ability to prepare a Zn−Cr LDH with decavanadate at pH 6.5, provided the preparation begins with a solution of decavanadate previously adjusted to pH 4.5, allows us some variation in the nature of the matrix of the LDH. Zn−Al LDHs, for example, are known to precipitate in a range between pH 6 and pH 10, with particularly good crystallinity obtained close to pH 7.[18] Figure 2a shows a PXRD pattern of the product, obtained from the direct synthesis of Zn−Al (with ratio 2) with decavanadate precipitated at pH 4.5. Two phases are observed. The first is mainly a Zn−Al LDH structure with $[V_{10}O_{28}]^{6-}$ between the layers. (006) and (009) reflections are present at 5.88 and 3.90 Å, although an 003 reflection is not observed. An additional phase is also present which is characterized by a broad peak at 9.4 Å, (10°/2θ) which is due to the formation of Zn and/or Al polyoxovanadate.[12,17] Good crystallinity of a Zn−Al LDH with decavanadate is obtained, when the coprecipitation is performed at pH value 6.5. The (003) reflection is clearly observed at 11.85 Å, along with the other reflections (Figure 2b). From the d_{110} value of 1.53 Å we estimate,[18] using the relationship $a = 2d_{110}$, that the layers are of approximate composition Zn:Al = 2. In particular, the intensity of the broad peak is decreased. If no initial adjustment to pH 4.5 of metavanadate solution is made, the coprecipitation at 6.5 indicates only a very small amount of the layered structure. The main product is a Zn−Al and/or metavanadate salt (Figure 2c).

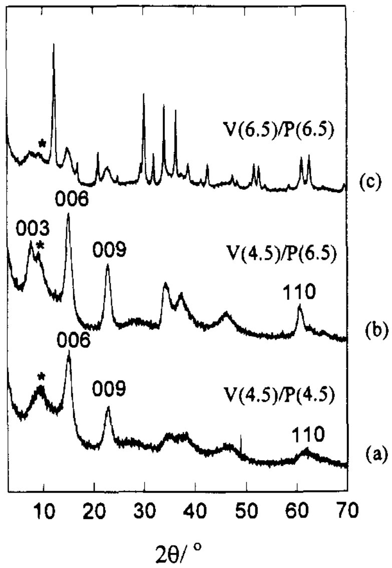

Figure 2. PXRD patterns of Zn−Al LDHs. pH conditions are similar to those in Figure 1. Parts a and b involve an initial vanadate solution at pH 4.5 with precipitation at pH 4.5 and pH 6.5, respectively. Part c involves precipitation at pH 6.5 with no prior equilibration at 4.5. (003) and (110) reflexions are significantly better resolved in part b compared to part a. An asterisk indicates an impurity phase (see text).

The presence of $[V_{10}O_{28}]^{6-}$ at pH 4.5 and pH 6.5 is confirmed by FT-IR spectroscopy. The LDH resulting at pH 4.5, contains new bands at 960, 814, 744, 560, and 512 cm^{-1}. The band at 960 cm^{-1} can be ascribed to the symmetric stretching mode of the terminal V=O groups ($\nu_{V=O}$), while the bands between 800 and 500 cm^{-1} may be assigned to antisymmetric and symmetric stretching modes of V−O−V chains.[20] These bands coincide with those reported for pillared Mg−Al and Ni−Al LDHs by $(V_{10}O_{28})$ anions[8,13,21] and prepared by exchange or rehydration methods. The spectrum of a sample prepared at pH values between 8.5−10.5, indicates that a different polyoxovanadate species is formed between the layers. Broad bands at 900, 780, and 505 cm^{-1} are observed, and may indicate the presence of polymeric $[VO3]_n^{n-}$.[13] As in the case of Zn−Cr system, FT-IR of the Zn−Al coprecipitated at pH 4.5, shows the characteristic bands of expanded structure with decavanadate anions. At pH 6.5, however, no bands of decavanadate are observed. A main band at 800 cm^{-1} is recorded and may indicate the formation of a metavanadate salt. From TGA data and chemical analysis, the sample prepared at pH 4.5 has the chemical formula $[Zn_{0.67}Cr_{0.33}(OH)_2](V_{10}O_{28})_{0.055}\cdot 1.04H_2O$.

It is likely, therefore, that provided the precipitation of the LDH sheets is possible at or below pH 6.5, $[V_{10}O_{28}]^{6-}$ anions may be incorporated directly into a variety of LDH hosts.

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