

Preparation of Porous Chromia-pillared Titanoniobate

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The first chromia-pillared titanoniobate is prepared through the reaction of a $\text{Cr}(\text{OAc})_3$ aqueous solution with a colloidal suspension of layered tetramethylammonium titanoniobate followed by calcination in N_2 ; the resultant material is porous with a surface area of $122.4 \text{ m}^2 \text{ g}^{-1}$, a narrow pore-size distribution and thermal stability beyond $500 \text{ }^\circ\text{C}$.

The synthesis of porous, thermally stable materials by calcining intercalated inorganic polyhydroxy-cation precursors in layered solids, such as smectite clays, layered phosphates and metal oxides, is an attractive approach for the formation of new materials for use in separation, sorption, conduction and catalysis applications.^{1,2} Silica and alumina are the most common pillars used, although other transition metal hydroxide oligomers such as those of Ni, Cr and Fe have also been used as pillaring agent for clays and phosphates and lead to materials with different characteristics.³ However, the non-swelling nature of the layer metal oxides prevents the facile ion exchange of large inorganic oxo cations, and so far only a few papers have been reported concerning the pillaring of the layered metal oxides mainly with silica and alumina.⁴⁻⁷

We now report the preparation of chromia-pillared layered titanoniobate through the reaction of $\text{Cr}(\text{OAc})_3$ solution with a colloidal suspension of layered tetramethylammonium titanoniobate. Oligomeric Cr^{3+} species intercalated titanoniobate with high crystallinity and a large interlayer distance ($d_{002} = 2.32 \text{ nm}$) was thus obtained. After calcination under an N_2 flow at $400 \text{ }^\circ\text{C}$, the first chromia-pillared layer titanoniobate with a

rather high BET surface area of $122.4 \text{ m}^2 \text{ g}^{-1}$ and a narrow pore-size distribution was obtained.

Layered KTiNbO_5 was prepared by the solid-state reaction of a stoichiometric mixture of K_2CO_3 , TiO_2 and Nb_2O_5 powder at $1100 \text{ }^\circ\text{C}$ for 24 h, and was then exchanged with HCl to give HTiNbO_5 . By adding an aqueous solution of propylamine to HTiNbO_5 and stirring the mixture at room temperature, a propylamine intercalated titanoniobate suspension was obtained, which was further exchanged with tetramethylammonium chloride to form a colloidal suspension of layered tetramethylammonium titanoniobate. An aqueous solution of $\text{Cr}(\text{OAc})_3$ was then added to the above colloidal suspension

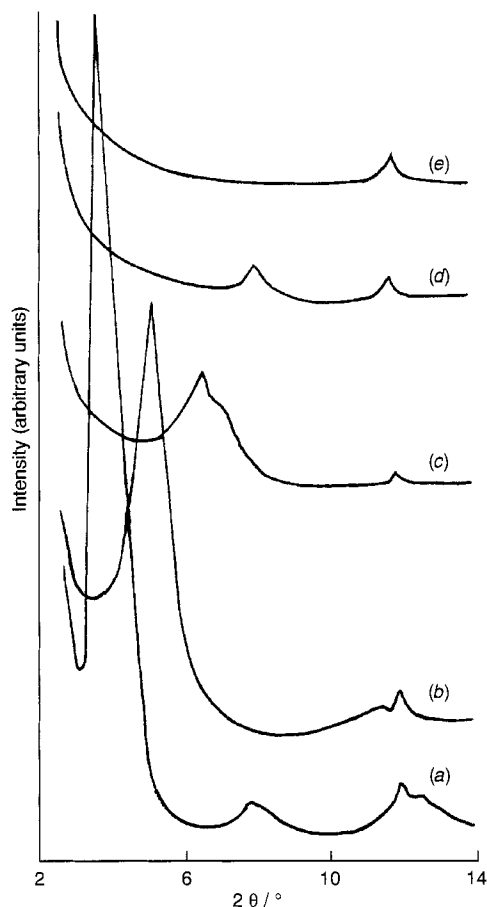


Fig. 1 $\text{Cu-K}\alpha$ X-ray diffraction patterns of: (a) Cr^{3+} oligomers intercalated titanoniobate; (b) as (a) calcined in N_2 at $200 \text{ }^\circ\text{C}$ for 2 h; (c) at $400 \text{ }^\circ\text{C}$ for 2 h, (d) at $500 \text{ }^\circ\text{C}$ for 2 h; and (e) at $600 \text{ }^\circ\text{C}$ for 2 h

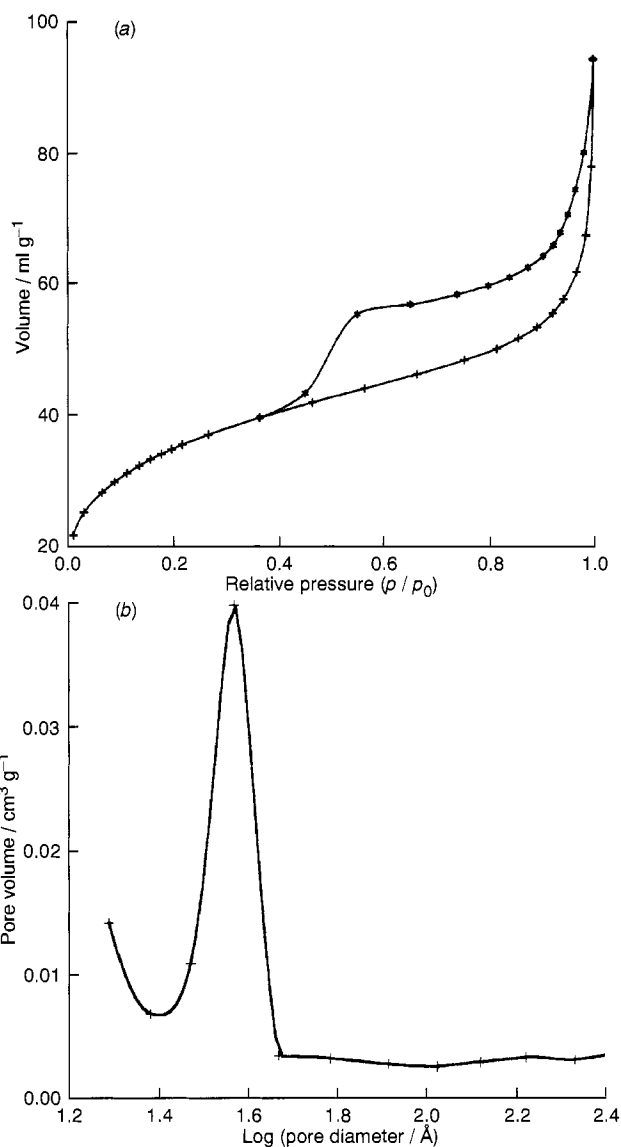


Fig. 2 (a) Adsorption-desorption isotherm of N_2 of the chromia-pillared layered titanoniobate ($400 \text{ }^\circ\text{C}$, N_2). +, adsorption; *, desorption. Volume of N_2 quoted at STP. (b) Pore-size distribution of chromia-pillared layered titanoniobate ($400 \text{ }^\circ\text{C}$, N_2).

with stirring, first at 30 °C and then at 60 °C for 1 d each, followed by heating under reflux for 2 d. The resultant was centrifuged, washed and air dried at room temperature, followed by calcination.

Fig. 1 shows the X-ray diffraction patterns of the product calcined in N₂ flow as a function of the calcination temperature. The HTiNbO₅ prepared has an interlayer distance of 0.87 nm ($2\theta = 10.1^\circ$, attributable to the [002] reflection of HTiNbO₅⁸). After intercalation by Cr³⁺ oligomers this peak disappears, and a new peak appears near $2\theta = 3.8^\circ$ ($d_{002} = 2.32$ nm), along with its higher-order counterparts. With increasing of the calcination temperature from 200 to 400 °C this peak gradually shifts to a higher 2θ value and becomes broad, and the interlayer distance decreases from 1.70 to 1.34 nm. TG-DTA analyses show that a strong exothermic peak along with a mass loss can be seen at 341 °C, which implies that after calcination of the resultant product at 400 °C, Cr³⁺ oligomers have already been decomposed and converted to a Cr₂O₃ (binding energy, E_b of Cr $2p_{3/2} = 577.5$ eV) pillar existing in the interlayer. Upon heat treatment at 500 °C the interlayer distance further decreases to 1.08 nm, and treatment at 600 °C leads to the collapse of the pillared structure. Similar results are obtained for the product calcined in air at different temperatures. The main difference is that a much smaller interlayer distance is observed for the product calcined in air. XPS results confirm that a small part of Cr⁶⁺ ($E_b = 579.1$ eV) existed in this sample, hence we assume that the existence of CrO₃ as a pillar instead of as part of the Cr₂O₃ leads to the decrease of the interlayer distance.

The N₂ adsorption-desorption isotherm of the chromia-pillared titanoniobate is shown in Fig. 2(a). The type H3 hysteresis loop is associated with the aggregation of plate-like particles giving rise to slit-shaped pores.⁹ The pore-size distribution is mainly concentrated in the range 3.0–4.6 nm with an average pore diameter of 3.4 nm [see Fig. 2(b)]. The surface area of the chromia-pillared layer titanoniobate calcined in N₂ is 122.4 m² g⁻¹ which is almost 70 times as large as the original

material KTiNbO₅ (1.8 m² g⁻¹). In contrast, the specific surface area of the material calcined in air is only 73 m² g⁻¹, with a smaller pore volume.

Two types of acid sites are present in the materials as shown in the pyridine adsorption IR spectra by the appearance of bands at 1546 and 1455 cm⁻¹, characteristic of Brønsted and Lewis acid sites respectively. The NH₃ temperature-programmed desorption results reveal that the total acid amount is *ca.* 528 μmol g⁻¹, which is much greater than that of silica-pillared titanoniobate.¹⁰ It is found that the acid content of the sample increases with increasing of the surface area.

A transmission electron micrograph and the corresponding lattice diffraction pattern of the pillared titanoniobate show the clear slit-like pores and high crystallinity of the material.

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