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Synthesis and characterization of porous chromia-pillared layered titanoniobate†

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Oligomeric chromium(III)-intercalated titanoniobate has been prepared by the intercalation of propylamine into $KTiNbO_5$ followed by substitution of propylammonium for tetramethylammonium and finally refluxing with an aqueous solution of $Cr(O_2CMe)_3$. The first chromia-pillared layered titanoniobate was then obtained by calcination of oligomeric chromium(III)-intercalated titanoniobate at 400 °C in a flow of N_2. Characterization of chromia-pillared titanoniobate revealed that the material has the porous layered structure with a Brunauer–Emmett–Teller surface area of 122.4 $m^2\ g^{-1}$ and an interlayer distance of 13.4 Å as well as a narrow pore-size distribution in the range 30–46 Å. The layered structure can be retained up to 500 °C. However, calcination of the oligomeric chromium(III)-intercalated titanoniobate in air at the same temperature led to a product with a low surface area and a small interlayer space. X-Ray photoelectron studies indicate the existence of different states of chromia in the products obtained in the different atmospheres. The IR spectra of the pyridine-adsorbed material and the ammonia temperature-programmed desorption profile demonstrate the presence of a large amount of acid sites with medium strength on the surface of the new chromia-pillared material. Isopropyl alcohol decomposition confirms the existence of only acid sites in the sample.

The formation of porous, thermally stable materials by calcining intercalated polyoxycation precursors in layered solids is an attractive approach for obtaining new materials applicable to separations, ion exchange, conduction as well as catalysis.[1,2] Polyhydroxy cations of silica and aluminium are the most common pillars used for preparing pillared smectite clays, phosphates or other pillared layered materials with different characteristics.[3–5] Chromium is one of the most important components in catalysis. Chromia-pillared materials are of particular interest because the interlayer pillaring agent itself is catalytically active.[6] It was first investigated as a pillar for smectite clay by Brindley and Yamanaka[7] in 1979. Chromia-pillared montmorillonite exhibited a larger gallery height than those of zirconium- and aluminium-pillared clays accompanied by a greater activity than that of commercial chromia catalyst for the dehydrogenation of cyclohexane to benzene.[8] Recently, layered α-tin[9] or -zirconium[10] phosphates have also been pillared by chromia and showed marked enhancements of acidities with respect to the original phosphates.

The compound $KTiNbO_5$ is a member of the family of layered alkali-metal–transition-metal oxides in which the alkali-metal ions lie between layers built up from zigzag chains of edge-sharing MO_6 octahedra ($M = Ti$ or Nb). The lamella structure is susceptible to topotactic reactions such as proton exchange and intercalation of alkylamines.[11] Its protonic form, $HTiNbO_5$, appears to be the strongest Brønsted acid among the members of the series and shows a noticeable photocatalytic activity for the evolution of H_2 from aqueous solution.[12] In previous works new porous, layered pillared titanoniobates have been prepared by this group through intercalations of octameric siloxane[13] and aluminium Keggin[14] cations with direct reaction or stepwise exchange processes. In addition to the great increase in surface area, the amount of the acid site of the silica-pillared titanoniobate is noticeably large.

In the present study, oligomeric chromium(III)-intercalated titanoniobate is obtained by preswelling layered titanoniobate with *n*-propylamine followed by forming a colloidal suspension of tetramethylammonium titanoniobate and finally refluxing with aqueous chromium acetate. Calcination of the product at 400 °C in a flow of N_2 results in the first chromia-pillared titanoniobate with a porous, thermally stable layered structure. The new material has a narrow pore-size distribution in the range 30–46 Å and a great increase in acidity compared to that of the previous silica-pillared sample.

Experimental

Preparation

The compound $KTiNbO_5$ was prepared by the solid-state reaction of a stoichiometric mixture of K_2CO_3, TiO_2 and NbO_5 powders at 1100 °C overnight. Cation-exchange reaction was carried out with 2 mol dm^{-3} HCl at 60 °C for 4 h to give $HTiNbO_5$. *n*-Propylamine-intercalated titanoniobate was obtained by adding an aqueous solution (27 cm^3) of 0.1 mol dm^{-3} *n*-propylamine to $HTiNbO_5$ (1 g) with stirring at 25–30 °C for 24 h. Addition of tetramethylammonium chloride (7.5 cm^3, 3 mol dm^{-3}) and stirring at room temperature for 4 d led to the formation of a colloidal suspension of layered tetramethylammonium titanoniobate. This was treated with an aqueous solution of $Cr(O_2CMe)_3$ (308 cm^3, 0.1 mol dm^{-3}) at room temperature and 60 °C each for 1 d followed by refluxing for 2 d. After reflux the resultant was centrifuged, washed and air dried at room temperature. Calcining the above product at 400 °C in a flow of N_2 gave the chromia-pillared titanoniobate.

Characterization

The basal spacing of the oriented sample was evaluated by powder X-ray diffraction (XRD) measurement on an XD-3A X-ray diffractometer with Cu-Kα radiation and nickel filter using a cast film. The Brunauer–Emmett–Teller surface area and pore-size distribution analyses were carried out by nitrogen adsorption–desorption measurement at 77 K on Micromeritics ASAP-2000 equipment. The sample was evacuated at 350 °C for pretreatment. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C elemental microanalyser; Ti, Nb and Cr in the chromia-pillared material were measured by X-ray fluoroscopy (XRF). The TG-DTA analyses were performed on a Rigaku thermoanalyser at a heating rate of 10 °C min^{-1} using α-Al_2O_3 as reference. Infrared spectra were

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

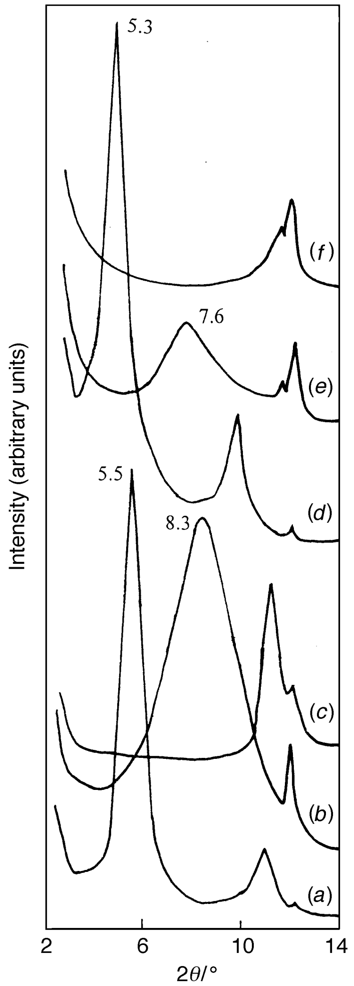

Fig. 1 X-Ray diffraction patterns of (*a*) *n*-propylamine-intercalated titanoniobate; (*b*) as (*a*), calcined at 200 °C in air; (*c*) as (*a*), calcined at 400 °C; (*d*) tetramethylammonium-intercalated titanoniobate; (*e*) as (*d*), calcined at 300 °C in air; (*f*) as (*d*), calcined at 400 °C

recorded on a Nicolet 5DX FT-IR spectrophotometer for skeleton analysis using KBr pellets. Self-supporting wafers were used for recording IR spectra upon pyridine adsorption in order to evaluate the nature and strength of the acidic sites of the samples. The total acid amount was evaluated by temperature-programmed desorption (TPD) of ammonia. X-Ray photoelectron spectra (XPS) were recorded with an ESCALAB MK-II spectrometer equipped with an Mg-Kα X-ray excitation source. The carbon 1s peak at 284.6 eV was used as the reference for binding energies. Decomposition of Pr^iOH as a probe reaction was carried out in a convenient flow reactor at 260 °C. The catalyst (70 mg) was preheated in a flow of N_2 at 300 °C for 2 h prior to the introduction of reactant (weight hour space velocity = 4.66 h^{-1}). The decomposition products were analysed by gas chromatography using a Porapak-T packed column at 135 °C with a thermal conductivity detector.

Results and Discussion

n-Propylamine- or tetramethylammonium-intercalated titanoniobate

The $KTiNbO_5$ obtained and its proton-exchanged form $HTiNbO_5$ showed XRD patterns coincident with those in ref. 15. Fig. 1 shows the X-ray diffraction patterns of titanoniobates intercalated with different species and their variations upon heat treatments. Reaction of $HTiNbO_5$ with *n*-propylamine resulted in the formation of an *n*-propylamine-intercalated $HTiNbO_5$ with an expanded interlayer distance of 16.1 Å which corresponds to the [002] reflection at 2θ 5.5° as shown in Fig. 1(*a*). Calcination of the intercalated titanoniobate at 200 °C led to a shift of the [002] reflection peak from 2θ 5.5 to 8.3°, suggesting a decrease in the interlayer distance, whereas calcining at 400 °C for 4 h resulted in disappearance of the [002] reflection peak of *n*-propylamine-intercalated layered titanoniobate as shown in Fig. 1(*c*). It is concluded that the layered structure of the intercalated $HTiNbO_5$ is destroyed by the decomposition of *n*-propylamine combined with the fact that the intercalated *n*-propylamine decomposes at 347 °C during the thermal analysis.

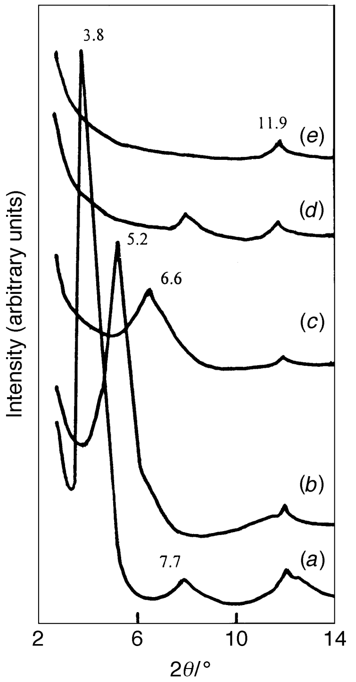

Fig. 2 X-Ray diffraction patterns of (*a*) titanoniobate intercalated with chromium(III) oligomers and calcined in N_2 at 200 (*b*), 400 (*c*), 500 (*d*) and 600 °C (*e*)

Further reaction of *n*-propylamine-intercalated $HTiNbO_5$ with NMe_4Cl led to the formation of a colloidal suspension of tetramethylammonium-exchanged layered titanoniobate in which the interlayer distance is expanded to 16.7 Å corresponding to the [002] reflection shown at 2θ 5.3° in Fig. 1(*d*). Like its precursor, the tetramethylammonium-intercalated $HTiNbO_5$ lost its pillars along with the destruction of the layered structure on heat treatment at 400 °C due to the decomposition of intercalated organics as demonstrated in Fig. 1(*f*). Thermal analysis confirmed the decomposition of intercalated tetramethylammonium at about 388 °C.

Oligomeric chromium(III)-intercalated titanoniobate

Reaction of the above colloidal suspension of tetramethylammonium-intercalated titanoniobate with chromium acetate resulted in the formation of polyoxycations of chromium *in situ* on the colloidal surface[9] of the intercalated layered titanoniobate and substitution of tetramethylammonium. An oligomeric chromium(III)-intercalated titanoniobate with a highly crystallized layered structure was obtained. Fig. 2 shows the diffraction patterns of this material. The interlayer distance in the oligomeric chromium(III)-intercalated sample is 23.2 Å corresponding to the [002] reflection peak at 2θ 3.8°. By subtracting the $TiNbO_5^-$ layer thickness of 6.1 Å,[16] an interlayer space of 17.1 Å is found on pillaring titanoniobate with chromium(III) oligomers. Elemental microanalyses (C, H, N) showed the existence of only C and H in the sample, indicating complete exchange of tetramethylammonium ions by chromium(III) oligomer. In Fig. 3 the IR spectrum of the chromium(III) oligomer-intercalated material shows bands at 1546 and 1454 cm^{-1} which can be assigned to the asymmetric and symmetric

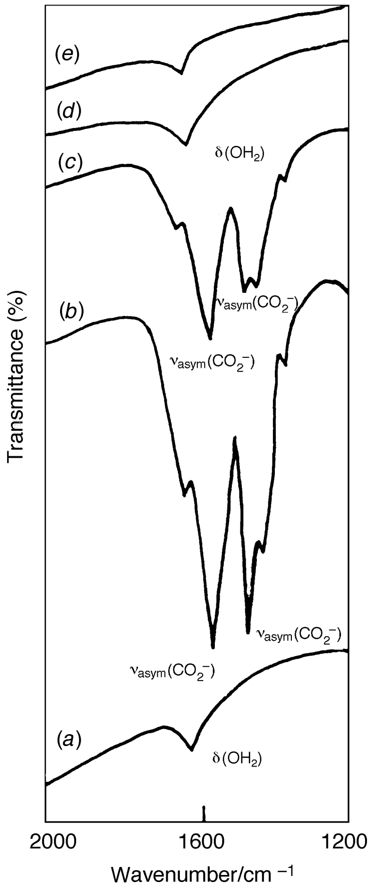

Fig. 3 Infrared spectra of (*a*) $KTiNbO_5$, (*b*) titanoniobate intercalated with chromium(III) oligomers and calcined at 200 °C in air (*c*), 400 °C in air (*d*) and 400 °C in N_2 (*e*)

stretching vibrations of CO_2^-,[17,18] respectively. It suggests that the intercalated oligomeric chromium(III) species may exist as a poly(hydroxyacetato) species like those believed to exist in α-tin phosphate.[9]

Chromia-pillared layered titanoniobate

The inorganic chromium(III)-pillared titanoniobate was then prepared by calcination of the poly(hydroxyacetato)-intercalated titanoniobate at 400 °C in a flow of N_2. The chromia-pillared material obtained contains 25.6% (w/w) of Cr_2O_3. The interlayer distance of the new material is 13.4 Å, corresponding to the [002] reflection at 2θ 6.6°. The X-ray diffraction patterns of the oligomeric chromium(III)-intercalated titanoniobate varied upon calcination at different temperatures as illustrated in Fig. 2. The [002] reflection peak of the chromium(III) oligomer-intercalated titanoniobate shifted to 5.2° at 200 °C corresponding to an interlayer distance of 17.0 Å where the organic acetate group was still in the interlayer space as shown by the IR spectrum in Fig. 3(*c*). A further increase in the calcination temperature to 400 °C resulted in a decrease in the interlayer distance to 13.4 Å corresponding to a pillar height in the interlayer of titanoniobate of 7.3 Å.

Decomposition of the organic acetate leaves inorganic chromia pillars in the interlayer of titanoniobate. A strong exothermic peak together with a significant weight loss appeared at about 341 °C in the TG-DTA analysis which represents decomposition of the intercalated chromium(III) oligomeric species. The IR spectrum [Fig. 3(*d*)] of the sample treated at 400 °C also supports this conclusion, the absorption bands at 1546 and 1454 cm^{-1} caused by stretching vibrations of CO_2^- having disappeared. The band at 1630 cm^{-1} is attributed to the H–O–H bending vibration.[17] The results of the XPS study on the sample treated at 400 °C in a flow of N_2 showed a chromium $2p_{\frac{3}{2}}$ peak at a binding energy of 577.5 eV which indicates that the chromia pillar exists as Cr_2O_3[19] in the interlayer of the material. The layered structure may be retained at 500 °C in a nitrogen atmosphere with a small decrease in interlayer distance. However, calcination at 600 °C led to collapse of the layered structure of the chromia-pillared titanoniobate [see patterns (*d*) and (*e*) in Fig. 2].

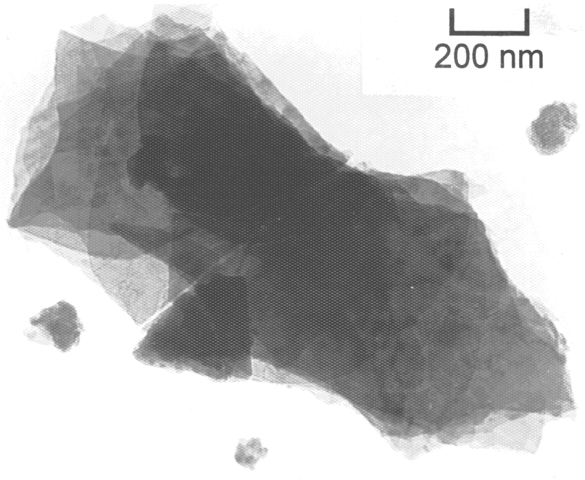

Fig. 4 Transmission electron micrograph of chromia-pillared titanoniobate (400 °C, N_2) illustrating the layered structure of the plate-like particle. Magnification = ×50 000

A similar phenomenon was observed upon calcination of the material in air, however a much smaller interlayer distance than that in a flow of N_2 at the same temperature was obtained. The sample treated at 400 °C, for instance, has an interlayer distance of only about 10.8 Å. The results of the XPS study showed a chromium $2p_{\frac{3}{2}}$ peak at a binding energy of 577.4 eV accompanied by a shoulder at 579.1 eV which can be assigned to a Cr^{6+} species.[19] Some CrO_3 is probably formed upon treating the sample in air.

Porosity of the chromia-pillared titanoniobate

The synthesized chromia-pillared titanoniobate has a porous layered structure, as is demonstrated by the significant increase in surface area of the material and the appearance of a hysteresis loop in the nitrogen adsorption–desorption isotherm.[20] The surface area of the new material is as high as 122.4 $m^2\ g^{-1}$ and the micropore volume is 0.012 $cm^3\ g^{-1}$. On the contrary, the starting titanoniobate is actually non-porous (surface area of $KTiNbO_5$ is only 1.8 $m^2\ g^{-1}$). A marked enhancement in microporosity is obtained by pillaring the layered titanoniobate with chromia. The hysteresis loop in the adsorption–desorption isotherm is of type H3 as classified by Sing *et al.*[21] It suggests a porous structure associated with aggregates of plate-like particles giving rise to slit-shape pores. Additionally, the transition electron micrograph of the obtained material revealed the layered structure and plate-like particles (Fig. 4). The pore-size distribution analysis showed that most of the pore sizes are distributed in a narrow range of 30–46 Å with maximum distribution at 34 Å.[20] The accessible colloidal surface of intercalated titanoniobate permits growth of polyhydroxyacetato-chromium(III) oligomers in an ordered way, which on calcination give rise to porous oxide-pillared materials of narrow pore range.

By comparison, the material calcined at 400 °C in air gives rise to a material with a low surface area of 73.0 $m^2\ g^{-1}$ which is much less than that of the material calcined in a flow of N_2. It is not in agreement with that observed in chromia-pillared α-tin phosphate where the air-treated sample has a larger surface area than that treated in N_2 due to the formation of some impurity phases by air calcining.[9]

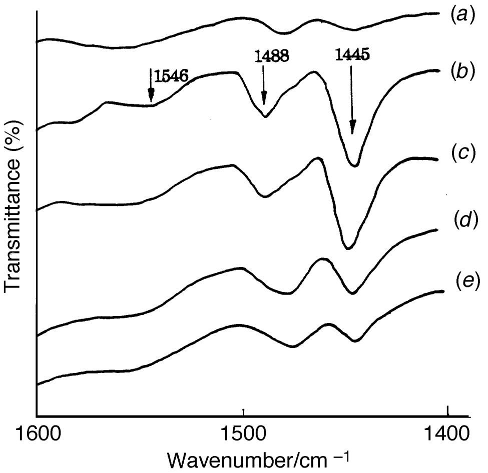

Fig. 5 Infrared spectra of pyridine adsorbed on chromia-pillared titanoniobate (400 °C, N_2): (*a*) background; evacuated at room temperature (*b*), 150 (*c*), 250 (*d*) and 350 °C (*e*) for the pyridine-adsorbed sample

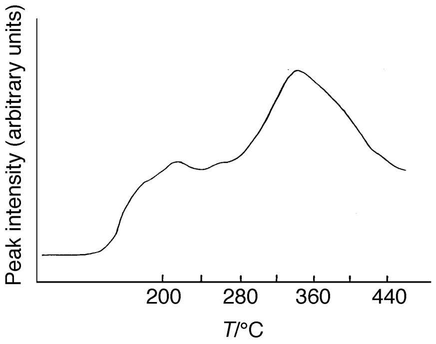

Fig. 6 The ammonia TPD profile of chromia-pillared titanoniobate (400 °C, N_2)

Acidity of the new pillared material

Fig. 5 shows the IR spectra of pyridine-adsorbed chromia-pillared titanoniobate. The bands at 1445 and 1546 cm^{-1} are attributed to the absorptions caused by Lewis-acid and Brønsted-acid sites, respectively.[22] The band at 1488 cm^{-1} is caused by pyridine absorbed on both the Lewis- and Brønsted-acid sites. After desorption at 350 °C only the band at 1445 cm^{-1} representing the Lewis-acid site can be observed. The ammonia TPD profile is shown in Fig. 6. Three main desorption peaks at 175, 220 and 340 °C represent the medium-strong acidity with 60, 92 and 376 $\mu mol\ g^{-1}$ acid, respectively. The total acid amount is *ca.* 528 $\mu mol\ g^{-1}$, much greater than that of silica-pillared titanoniobate.[13] The greater acid amount is considered to arise from the greater acidity of the Cr_2O_3 pillar.

Decomposition of Pr^iOH was carried out over the synthesized chromia-pillared titanoniobate to identify the catalytic property of the new material. A conversion of 96.8% is reached at which only the dehyrdration products were detected. Dehydration of Pr^iOH suggests that the porous chromia-pillared layered titanoniobate is a kind of solid acid catalyst on which only acid sites exist.

Acknowledgements

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