

Highly Thermostable, Porous, Layered Titanoniobate Pillared by Silica

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The first silica-pillared titanoniobate has been prepared by firstly intercalating layered titanoniobate with $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ and subsequently thermally removing the interlayered organics, the resulting pillared material is porous and has a high thermal stability beyond 750 °C.

Layered compounds such as clays and four-valent acid-form metal phosphates can be intercalated with polar organic molecules and inorganic cations. The layered compound becomes porous upon pillaring and has a significant surface area as well as sorptive and catalytic properties.¹⁻⁴ A series of lamellar protonic oxides such as $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$, $\text{H}_2\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$, $\text{H}_3\text{Ti}_5\text{NbO}_{14} \cdot \text{H}_2\text{O}$, $\text{HTi}_2\text{NbO}_7 \cdot \text{H}_2\text{O}$ and HTiNbO_5 are characterized by their ability to incorporate amines to form intercalated derivatives owing to their acid properties.^{5,6} Among these different oxides, HTiNbO_5 appears as the strongest acid since it can intercalate nitrogen compounds characterized by a rather low $\text{p}K_{\text{a}}$ close to 6.⁷ Much attention has been devoted to research in this field because of its potential in separation, sorption, conduction and catalysis. In general, these organically pillared structures suffer from the thermal instability of the intercalated organic component, which limits their use in catalysis. An attempt was then made to prepare thermostable structures pillared by inorganic oxide.⁸ Since TiO_2 and Nb_2O_5 have several significant and distinctive properties as catalyst supports or catalysts, TiO_2 and Nb_2O_5 -based catalysts become an attractive subject of many scientific studies.⁹⁻¹² However, compared to Al_2O_3 and SiO_2 , TiO_2 and Nb_2O_5 have weaker acidity and relatively lower surface area at high temperatures. Of interest here is to prop open the layered titanoniobate (KTiNbO_5) with thermal stable inorganic pillars to form porous materials. Here, we report that $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ can be exchanged into layered titanoniobate to form an intercalate with an interlayer distance of 18.4 Å, calcination of this intercalate in air gives rise to the first porous silica-pillared layered titanoniobate with a high thermal stability above 750 °C.

KTiNbO_5 was prepared as a white solid by solid-state reaction of an intimate mixture of K_2CO_3 , TiO_2 and Nb_2O_5 in the molar ratio of 1 : 2 : 1 at 1100 °C overnight.¹³ The obtained KTiNbO_5 was then stirred in HCl (2 mol dm^{-3}) at 60 °C for 4 h to give HTiNbO_5 . HTiNbO_5 powder was added, under stirring, to a freshly-prepared 10 wt% aqueous solution of

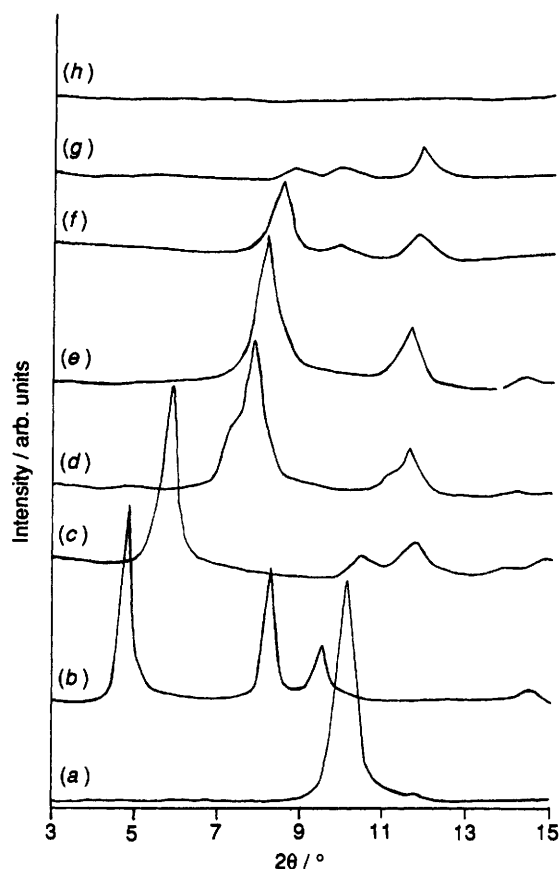


Fig. 1 Cu-K X-ray diffraction patterns of (a) HTiNbO_5 ; and $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ intercalated titanoniobate (b) air-dried at 50 °C, (c) calcined in air at 250 °C for 2 h and (d) 400 °C, 2 h, (e) 550 °C, 24 h, (f) 650 °C, 2 h, (g) 750 °C, 2 h, (h) 850 °C, 2 h

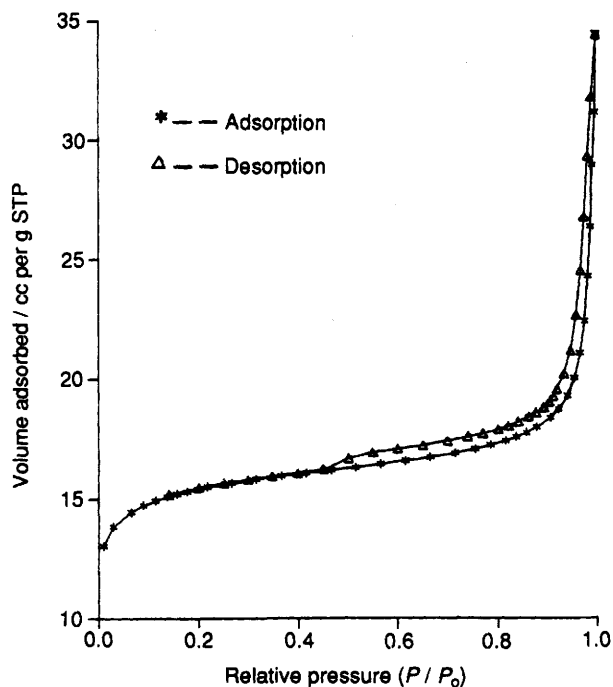


Fig. 2 Adsorption-desorption isotherm of N_2 on the silica-pillared titanoniobate (550 °C, 24 h); (*), adsorption; (Δ), desorption

$NH_2(CH_2)_3Si(OEt)_3$ (Si:Ti = 10:1). The mixture was refluxed for 6 days, followed by centrifuging and washing with distilled water, and air-dried at 50 °C. Fig. 1 shows the X-ray diffraction patterns of the resulting solid as a function of the calcination temperature along with the starting material $HTiNbO_5$. The $HTiNbO_5$ prepared has an interlayer distance of 8.7 Å. Upon treatment with the aqueous solution of $NH_2(CH_2)_3Si(OEt)_3$, the peak at $2\theta = 10.1^\circ$ ($d = 8.7$ Å) attributable to the [002] reflection of the host layer phase disappeared, while a new diffraction peak appeared near $2\theta = 4.8^\circ$ ($d = 18.4$ Å) along with its higher-order counterparts, indicating that the uptake of $NH_2(CH_2)_3Si(OEt)_3$ by layered titanoniobate can be attributed to its conversion into an intercalated phase. The organic molecules are intercalated as a bilayer structure with their NH_3^+ groups pointed to the $TiNbO_5^-$ layers. The formation of the NH_3^+ groups was confirmed by the presence of NH_3^+ vibrations in the FTIR spectrum of the solid product. It is noted that the [002] diffraction peak for the intercalated phase of $HTiNbO_5$ tends to become broad after heat treatment at 250 °C in air, which is due to the removal of water adsorbed during the intercalation and to the distortion of the intercalated organic species during calcination. With further increase in the heating temperature to 400 °C, the thickness of the intercalat layer rapidly decreases to 11.3 Å ($2\theta = 7.8^\circ$) with an accompanying appreciable decrease in C, H, N content as determined by elemental analysis, corresponding to the decomposition of the organic moiety. The associated TG and DTA analyses show that the interlayer organic ammonium ions begin to decompose at 306 °C. Therefore, after calcining the resultant intercalate in air at 550 °C for 24 h, the organics within the layers decomposed to form silica-like compounds acting as pillars to prop up the $TiNbO_5^-$ layers, and a silica-pillared material is obtained. Chemical analysis results confirm that there is no loss of silicon from the sample upon calcination. It can also be seen from Fig. 1 that the silica-pillared titanoniobate has a high thermal stability above 750 °C and collapses when heated at 850 °C.

N_2 adsorption-desorption isotherm for the silica-pillared material is shown in Fig. 2. $KTiNbO_5$ itself is non-porous, with



Fig. 3 TEM of $NH_2(CH_2)_3Si(OC_2H_5)_3$ intercalated titanoniobate

a very low BET surface area of $1.8\text{ m}^2\text{ g}^{-1}$, whereas, the pillared material is porous, having a relatively much higher specific surface area of $70\text{ m}^2\text{ g}^{-1}$. Moreover, NH_3 -TPD (temperature programmed desorption) results demonstrate that the resulting silica-pillared material has two acid sites, with the acid amount of 30 and $80\text{ }\mu\text{mol g}^{-1}$, respectively.

A transmission electron micrograph (TEM) of the intercalated titanoniobate is shown in Fig. 3. The layered nature of this material is clearly evident.

The layered titanoniobate does not swell in water due to its high charge density on the framework, and therefore, is not accessible to pillaring by conventional methods. The present results offer an alternative route to prepare highly thermally stable, porous, layered metal oxides pillared by inorganic oxides simply by treating layered titanoniobate with $NH_2(CH_2)_3Si(OEt)_3$ aqueous solution and subsequently pillaring by thermal removal of the interlayered organics.

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