Preparation and Characterization of TiO$_2$-pillared Layered HNb$_3$O$_8$

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Oligomeric titanium(IV) cation ($[Ti(OH)_x(H_2O)_y]^{z+}$)-intercalated niobate was prepared through a stepwise ion-exchange route, in which *n*-decylamine was employed as a preswelling agent and titanium isopropoxide as titanium source. Titania-pillared layered niobic acid was then obtained by calcining oligomeric titanium(IV) cation-intercalated niobate at 450 ℃ in air. Characterization of this pillared material indicated that the material had a porous layered structure with an interlayer distance of 1.38 nm and a BET (Brunauer-Emmett-Teller) surface area of 34 m^2 • g^{-1}. The layered structure was still retained after the pillared material was heated at 550 ℃.

Keywords　　　layered HNb$_3$O$_8$, titania, pillaring

Introduction

The layered compounds such as smectite clays, metallic phosphates and transition metal oxides pillared with inorganic oxides have been attracting more and more attention from both academic and industrial fields due to their potential applications in adsorption, separation, conduction and particularly catalysis.[1-7]

Niobates such as KNb$_3$O$_8$ and K$_4$Nb$_6$O$_{17}$, and the corresponding protonic oxides, HNb$_3$O$_8$ and H$_4$Nb$_6$O$_{17}$, are members of the family of layered transition metal oxides based on octahedral framework structure, in which K$^+$ or H$^+$ lies between layers built up from NbO$_6$ octahedral units.[8] Since the acid-base properties of Nb$_2$O$_5$ were examined and reported in 1980s,[9] hydrated Nb$_2$O$_5$ (*i.e.*, niobic acid) has been making an impact on its application as an unusual solid acid catalyst. However, niobic acid has a weaker acidity and a relatively lower surface area at high temperature. In order to increase the specific surface area and acidity of niobic acid calcined at high temperature, one approach is to prop the layered niobic acid with thermostable compounds to form porous materials. In our previous work,[10-12] pillared layered niobic acids with silica, alumina and chromia were prepared, and their structure and properties were investigated, respectively.

TiO$_2$ is one of the most important semiconducting oxides, and shows a remarkable photocatalytic activity in a series of reactions, such as decomposition of water into hydrogen and oxygen,[13] hydrogenation of propyne with water vapor,[14] decomposition of hazardous pollut- ants into innocuous substances,[15] *etc.* Moreover, it can be readily reduced to various stoichiometric or non-stoichiometric low-valent metal oxides, and the strong metal-support interaction (SMSI) was first found right in the catalyst of noble metal supported on TiO$_2$.[16] Therefore, in both "pillaring chemistry" and catalysis chemistry, TiO$_2$-pillared materials are particularly of interest. Over the past decades, the pillaring of clays with titania was extensively studied.[17-19] Recently, TiO$_2$ pillars have been constructed in the interlayers of several layered protonic oxides, such as H$_2$Ti$_4$O$_9$ and H$_4$Nb$_6$O$_{17}$, and the resultant materials were used in the photocatalytic decomposition of water.[20-22] However, the thermostability of these materials was not investigated. Generally speaking, the thermostability of a catalyst is dispensable to a photocatalytic process, but is very important for a high-temperature reaction (*i.e.*, non-photocatalytic reaction). In the present paper, we report the preparation and characterization of titania-pillared layered niobic acid (TiO$_2$-HNb$_3$O$_8$) with a porous structure and a high thermostability.

Experimental

Sample preparation

The starting material, layered potassium niobate (KNb$_3$O$_8$), was prepared according to the method reported in the literature.[8] The proton-exchange reaction was carried out in a solution of HNO$_3$ (7 mol/L) at room temperature for 3 d to give HNb$_3$O$_8$. *n*-Decyla mine-

intercalated niobate was obtained by adding HNb$_3$O$_8$ powder to an ethanol solution of *n*-decylamine (50% , in volume) with stirring at room temperature for one week. In order to prepare the titania-pillared layered niobic acid, acetic acid (160 mL) was first mixed with titanium isopropoxide (10 mL) and stirred for 1 h, then mixed with 240 mL of distilled water and stirred for 5 h, followed by adding *n*-decylamine-intercalated layered niobate (1.0 g) and stirring at room temperature for 7 d. The resultant solid product was separated, and then washed with distilled water three times and finally stayed in air at room temperature to dryness.

Characterization

XRD patterns of the obtained materials were recorded on a Shimadzu XD-3A diffractometer by using Cu Kα radiation at room temperature. Infrared spectra were measured on a Nicolet 5DX FT-IR spectrometer for skeleton analysis. Transmission electron micrographs (TEM) were obtained on a JEOL-200CX microscope. For TEM experiment, the sample was prepared by dipping copper grid coated with holey carbon films into a water suspension of the as-synthesized sample and allowing the grid to dry in air. Elemental analysis for C, H and N contents was carried out on a Perkin-Elmer 240C elemental analyzer. N$_2$ adsorption-desorption isotherms and BET specific surface area of the calcined sample were measured on a Micromeritics ASAP 2000 apparatus. The sample was degassed by evacuation at 300 ℃ to reach a vacuum below 0.4 Pa before the measurement.

Results and discussion

The layered structure of KNb$_3$O$_8$ has been well characterized.[8] In KNb$_3$O$_8$, units consisting of three NbO$_6$ octahedra are linked in the *b*-direction to form layers with the K$^+$ ions in the interlayer spaces. Both the layered compounds, KNb$_3$O$_8$ and the corresponding protonic oxides, HNb$_3$O$_8$, do not swell spontaneously in water due to their high charge densities in the frameworks. However, amines are readily intercalated into the interlayers of HNb$_3$O$_8$. In this work, the reaction of HNb$_3$O$_8$ with *n*-decylamine resulted in the formation of an *n*-decylamine-intercalated niobate with an expanded interlayer distance of 2.68 nm corresponding to the (010) diffraction at $2\theta = 3.3°$ as shown in Figure 1(a). The interlayer gallery height occupied by *n*-decylammonium ions has been calculated to be *ca.* 1.93 nm by subtracting the thickness of host layers (0.75 nm).[8] The interlayered *n*-decylammonium ions were thermally unstable, and the interlayer distance of the *n*-decylamine-intercalated niobate decreased to 1.25 nm ($2\theta = 7.1°$) after calcined in air at 350 ℃ for 2 h [Figure 1(b)]. The crystallinity also declined to a great extent as the (010) diffraction peak lost its intensity and became broad. Further calcination at 450 ℃ for 2 h led to the disappearance of the (010) diffraction peak [Figure 1(c)] and the collapse of the interlayer space. Figure 2 shows the

IR spectra of *n*-decylamine-intercalated niobate and its variation upon heating treatment. The sample before heating treatment showed the characteristic absorptions of the intercalated alkylamine in addition to those of the layered host. The IR absorption peak at 2962 cm^{-1} was attributed to CH$_3$ stretching vibration, while 2922 and 2853 cm^{-1} to CH$_2$ stretching vibrations, and 1473 cm^{-1} to CH$_2$ bending vibration, respectively. After the sample was calcined at 450 ℃, these peaks disappeared completely due to the decomposition and loss of the interlayered *n*-decylammonium ions. Moreover, CO$_2$ was formed and contributed a peak at 2338 cm^{-1}.
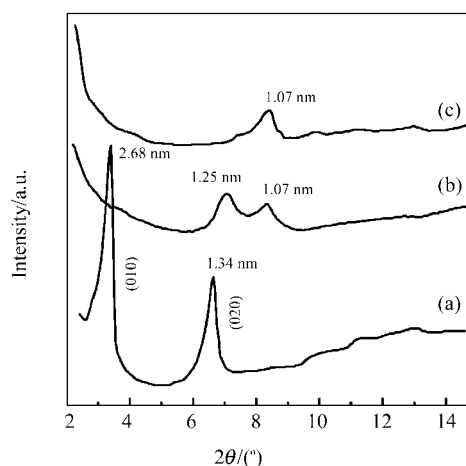

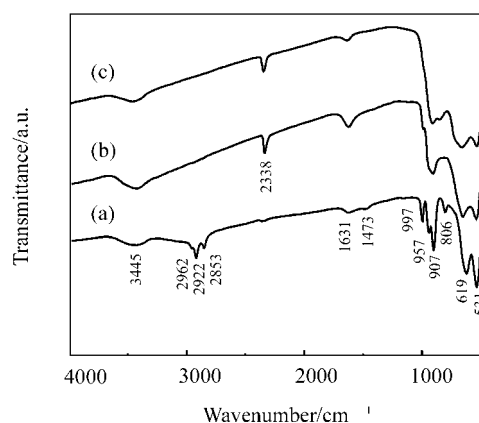**Figure 1** XRD patterns of *n*-decylamine-intercalated niobate at (a) room temperature, (b) 350 ℃, air, 2 h and (c) 450 ℃, air, 2 h.

Figure 2 IR spectra of *n*-decylamine-intercalated niobate at (a) room temperature, (b) 350 ℃, air, 2 h and (c) 450 ℃, air, 2 h.

A mixture of titanium isopropoxide, acetic acid and distilled water in a ratio of 1︰16︰24 (volume) generated a solution containing Ti(IV) polycation species, which was allowed to exchange with alkylammonium ions in the interlayers of the *n*-decylamine-intercalated niobate. As shown in Figure 3, this exchange reaction led to the formation of Ti(IV) polycation-intercalated layered niobate, in which the interlayer distance was contracted to 2.11 nm ($2\theta = 4.2°$). By increasing the

reaction time, the intensity of the diffraction peaks increased accordingly. Nevertheless, the position of all diffraction peaks remained unchanged. Both IR and elemental analysis results indicated that the previously interlayered *n*-decylammonium ions were completely exchanged out by Ti(IV) polycations after the exchange reaction, because the IR absorption peaks at 2962, 2922, 2853 and 1473 cm^{-1} fully disappeare, and no N was detected in the sample. On the other hand, concerning the form of Ti(IV) polycation species, since there were no characteristic absorption peaks corresponding to COO^- vibrations in the IR spectrum of the assynthesized sample, and no C was detected by the elemental analysis, it is reasonable to suggest that Ti(IV) polycations intercalated in the interlayers of the layered niobate contain no CH_3COO^- and have a formula of $[Ti(OH)_x(H_2O)_y]^{z+}$, in which *x*, *y*, and *z* are variables. This formula differed a bit from the form of $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$ obtained by Sat *et al.*[20, 21] Also, the interlayer distance of the as-synthesized $[Ti(OH)_x(H_2O)_y]^{z+}$-intercalated triniobate ($Nb_3O_8^-$) was obviously larger than that of $[Ti(OH)_x(CH_3CO_2)_y]^{z+}$-inter-calated hexaniobate ($Nb_6O_{17}^-$) becaus—e the first diffraction peak of the latter lied at *ca.* $2\theta = 6.0°$.[20]
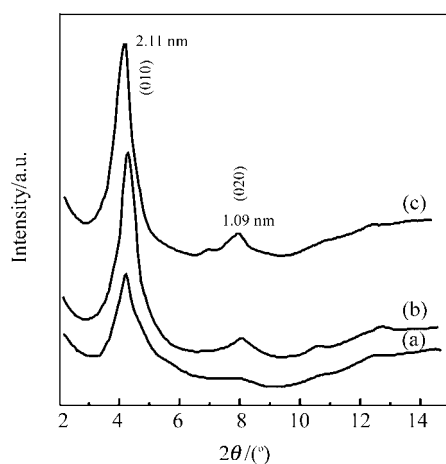

Figure 3 XRD patterns of the solid products obtained from the reaction between *n*-decylamine-intercalated niobate and Ti(IV) polycations at different reaction time: (a) 2 h, (b) 52 h and (c) 120 h.

Figure 4 shows XRD patterns of $[Ti(OH)_x(H_2O)_y]^{z+}$-intercalated niobate treated at different temperatures. The calcination of the intercalated niobate at 200 ℃ led to a great shift of the (010) diffraction peak from $2\theta = 4.2°$ to $5.3°$ [see Figure 4(a) and (b)] due to the dehydration of the interlayered $[Ti(OH)_x(H_2O)_y]^{z+}$. As the calcination temperature further increased from 200 to 350 ℃, this peak shifted slightly to a higher 2θ and its intensity was decreased gradually. Accordingly, the interlayer distance of the material was decreased from 1.67 to 1.45 nm. Upon heating treatment at 450 ℃ for 2 h, as a result, a titania-pillared niobic acid (TiO$_2$-HNb$_3$O$_8$) was formed with an interlayer distance of 1.38 nm. By subtracting the layer thickness of $Nb_3O_8^-$

(0.75 nm), the interlayer gallery height occupied by titania pillars was 0.63 nm, which was 0.11 nm larger than that in TiO$_2$-H$_4$Nb$_6$O$_{17}$ reported previously by Sato.[20] Compared with *n*-decylamine-intercalated niobate, the titania-pillared layered niobic acid is relatively thermal stable. As shown in Figure 4 and Figure 5, this titania-pillared material has a relatively high thermostability at a temperature higher than 550 ℃. Nevertheless, further calcination at 650 ℃ led to the collapse of the layered structure of the titania-pillared niobic acid.

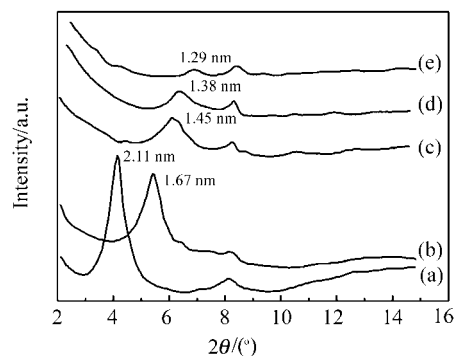**Figure 4** XRD patterns of $[Ti(OH)_x(H_2O)_y]^{z+}$-intercalated niobate at (a) room temperature, (b) 200 ℃, air, 2 h, (c) 350 ℃, air, 2 h, (d) 450 ℃, air, 2 h, and (e) 550 ℃, air, 2 h.
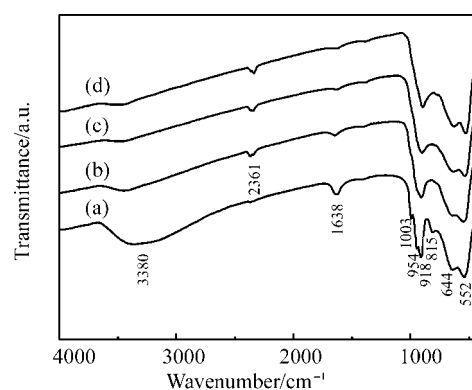
Figure 5 IR spectra of $[Ti(OH)_x(H_2O)_y]^{z+}$-intercalated niobate at (a) room temperature, (b) 350 ℃, air, 2 h, (c) 450 ℃, air, 2 h, and (d) 550 ℃, air, 2 h..

TEM was used to reveal the texture of titania-pillared layered niobic acid after calcination in air at 450 ℃ for 2 h. As shown in Figure 6, this pillared material exhibited a distinct lamellar structure, as expected.

The porosity and BET surface area of the titania-pillared layered niobic acid were calculated by means of N$_2$ adsorption-desorption isotherms as illustrated in Figure 7.

The starting material KNb$_3$O$_8$ itself is non-porous, with a BET surface area of 2.5 m$^2 \cdot$ g^{-1}. The pillared material, however, has a porous structure, as demonstrated by the appearance of a hysteresis loop in the N$_2$ adsorption-desorption isotherms. The BET specific surface area of this pillared material is 34 m$^2 \cdot$ g^{-1}. The enhancement of the surface area is due predominantly to

Layered HNb₃O₈

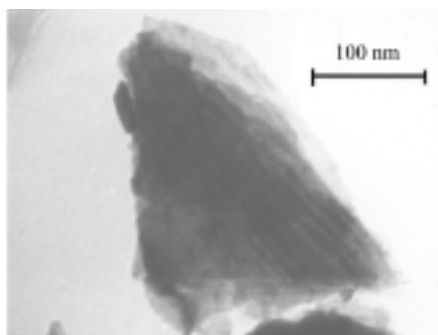*Chin. J. Chem.*, 2004, Vol. 22, No. 4 **343**

Figure 6 A TEM photo of titania-pillared layered niobic acid (450 ℃, air, 2 h).
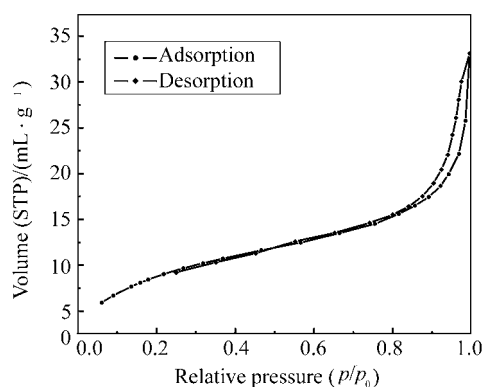

Figure 7 N$_2$ adsorption-desorption isotherms of titania-pillared layered niobic acid (450 ℃, air, 2 h).

a large number of pores in the interlayer spaces created by pillaring with titania. The adsorption isotherm recorded for this pillared material is of type IV in the BDDT classification. This type of isotherm is the characteristic of mesoporous materials with microporous contributions.[23] The hysteresis loop in the N$_2$ adsorption-desorption isotherms is of type H3 as classified by Sing *et al.*[24] The type H3 loop is often observed with aggregates of plate-like particles that give rise to slit-shaped pores. The average pore diameter of the as-prepared material was 4.74 nm.

Concluding remarks

By using a stepwise ion-exchange route, we have prepared titania-pillared layered niobic acid, which is a thermostable, porous and layered material. This pillared material has an interlayer spacing of 0.63 nm and a BET surface area of 34 m$^2 \cdot$ g^{-1} after calcined in air at 450 ℃ for 2 h. The interlayer spacing and BET specific surface area of the material are higher than those of alumina-pillared one, but lower than those of silica-pillared material. Since both the layered host and the pillars are semiconducting oxides, titania-pillared layered niobic acid is expected to show an excellent photocatalytic activity. This pillared material may also be used for various acid-catalyzed reactions because of the strong acidic properties of its layered host. The high thermal stability of the pillared niobic acid also enables its application as a catalyst support at a high-temperature. Moreover, this pillared material may combine the catalytic and conducting properties, leading to a new type of sensors.

References

1   Gil, A. L.; Gandia, M.; Vicente, M. A. *Catal. Rev.-Sci. Eng.* **2000**, *42*, 145.

2   Cheng, S.; Wang, T. C. *Inorg. Chem.* **1989**, *28*, 1283.

3   Landis, M. E.; Aufdembrink, B. A.; Chu, P.; Johnson, I. D.; Kirker, G. W.; Rubin, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 3189.

4   Ram, M. R. A.; Clearfield, A. *J. Solid State Chem.* **1994**, *112*, 288.

5   Ebina, Y.; Tanaka, A.; Kondo, J. N.; Domen, K. *Chem. Mater.* **1996**, *8*, 2534.

6   Shangguan, W.; Yoshid, A. *J. Mater. Sci.* **2001**, *36*, 4989.

7   Wang, X. G.; Hou, W. H.; Wang, X. S.; Yan, Q. J. *Appl. Catal. B* **2002**, *35*, 185.

8   Ledjar, R.; Borel, M. M.; Raveau, B. *Mater. Res. Bull.* **1985**, *20,* 1291.

9   Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Base*, Kodansha Press, Tokyo, **1989**, p. 60.

10   Hou, W. H.; Pen, B. C.; Yan, Q. J.; Fu, X. C. *J. Chem. Soc., Chem. Commun.* **1993**, 253.

11   Hou, W. H.; Yan, Q. J.; Fu, X. C. *Acta Chim. Sinica* **1994**, *52*, 877 (in Chinese).

12   Hou, W. H.; Chen, Y. S.; Guo, C. X.; Yan, Q. J.; Chen, Y. *Chin. J. Chem.* **1997**, *15*, 562.

13   Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.

14   Anpo, M.; Shima, T.; Kodama, S. *J. Phys. Chem.* **1987**, *91*, 4307.

15   Wold, A. *Chem. Mater.* **1993**, *5*, 280.

16   Tauster, S. J.; Fung, S. C.; Garten, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 170.

17   Yoneyama, H.; Haga, S.; Yamanaka, S. *J. Phys. Chem.* **1989**, *93*, 4833.

18   Bernier, A.; Admaiai, L. F.; Grange, P. *Appl. Catal.* **1991**, *77*, 269.

19   Ooka, C.; Akita, S.; Ohashi, Y.; Horiuchi, T.; Suzuki, K.; Komai, S.; Yoshida, H.; Hattori, T. *J. Mater. Chem.* **1999**, *9*, 2943.

20   Yanagisawa, M.; Uchida, S.; Fujishiro, Y.; Sato, T. *J. Mater. Chem.* **1998**, *8*, 2835.

21   Yanagisawa, M.; Uchida, S.; Yin, S.; Sato, T. *Chem. Mater.* **2001**, *13*, 174.

22   Tawkaew, S.; Yin, S.; Sato, T. *Int. Inorg. Mater.* **2001**, *3*, 855.

23   Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, Academic Press, London, **1982**, p. 4.

24   Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603.