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ORIGINAL ARTICLE

Intercalation behaviors of chiral titanium(IV) (triethanolaminato)-isopropoxide ($Ti(C_2H_4O)_3N(OCH(CH_3)_2)$) in protonated lamellar metal oxides and characterization of the intercalated resultants

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Abstract The intercalation behaviors of chiral titanium(IV) (triethanolaminato)-isopropoxide (the chemical formula is $Ti(C_2H_4O)_3N(OCH(CH_3)_2)$, abbreviated as TEAIP) in a series of layered protonated metal oxides (HNb_3O_8, $HTiNbO_5$, $HLaNb_2O_7$, $H_2Ti_4O_9$ and $H_2Ti_{2.8}Mn_{0.2}O_7$) were investigated. TEAIP could be intercalated into the interlayer spaces of layered HNb_3O_8 as well as $HTiNbO_5$, and as a result, two novel inorganic–organic hybrid nanocomposites, TEAIP-intercalated HNb_3O_8 and TEAIP-intercalated $HTiNbO_5$, were obtained,respectively. Based on the compositions of the intercalated compounds quantitatively estimated from TG-DTA data, the chemical formulas of the TEAIP-intercalated HNb_3O_8 and TEAIP-intercalated $HTiNbO_5$ were expressed as $(TEAIP)_{0.17}H_{0.83}Nb_3O_8$ and $(TEAIP)_{0.14}H_{0.86}TiNbO_5$, respectively. Neither $H_2Ti_4O_9$ nor $H_2Ti_{2.8}Mn_{0.2}O_7$ formed any intercalated phase through the exchange reaction between the layered protonated metal oxides and TEAIP; $HLaNb_2O_7$ could only accommodate a very limited amount of the guest molecules, giving rise to a TEAIP-partially intercalated layered product. The different intercalation behavior of TEAIP in the layered metal oxides was ascribed to the difference of these protonated metal oxides in acidity and the difference of the layered hosts in charge density. The competitively intercalation behavior between TEAIP and *n*-decylamine in the interlayer space of HNb_3O_8 as well as $HTiNbO_5$ was also investigated. Both TEAIP and *n*-decylamine could be simultaneously intercalated into HNb_3O_8, leading to two different guest-intercalated phases, although *n*-decylamine-intercalated phase was thermally unstable compared with the TEAIP-intercalated phase. In the case of $HTiNbO_5$, only *n*-decylamine-intercalated phase was formed. The different basicity and steric hindrance of the two kinds of guest molecules and different acidity of the two layered hosts were mainly responsible for the above results.

Keywords Intercalation · Titanium(IV) (triethanolaminato)-isopropoxide · Chiral · Chiral titanium(IV) (triethanolaminato)-isopropoxide-intercalated layered metal oxides

Introduction

A number of transition-metal oxysalts such as $K_2Ti_4O_9$, KNb_3O_8, $KTiNbO_5$ and $KLaNb_2O_7$, etc., show typical two-dimensional lamellar structure, which is comprised of semiconducting host layers and interlayered alkali cations [1]. Moreover, the layered transition-metal-oxysalt family has a lot of derivatives resulting from the partially replacement of elements of the host layers with other elements, providing an opportunity to fine-tune chemical and physical properties of the compounds by the proper selection of the constituent elements. The layered oxides have a potential to incorporate various guest molecules, and therefore can form an important class of intercalated nanocomposites. These materials may find many applications in some fields such as adsorption, separation, catalysis, electronics, magnetics and photochemistry. Unlike the smectite group of layered clay minerals, the layered transition-metal oxysalts usually have a higher layer-charge density, making the direct intercalation of bulky guest

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species difficult in the interlayer spaces. To introduce bulky guest molecules, the so-called "guest-exchange technique" has been the most commonly used [2–4]. Generally, one-step guest-exchange method is based on the acid–base reaction between the layered protonated oxides and the organic base. By using such a way, various amines and some porphyrins such as 5, 10, 15, 20-tetrakis (1-methyl-4-pyridinio) porphyin (H_2 tmpyp^{4+}) have been directly intercalated into the interlayer spaces of the layered metal oxides [2–8]. Further, the intercalated ammonium ions could be replaced by bulky organic cations or inorganic polycations [9–11].

Organo-transition-metal compounds show various special properties such as photochemical performance, biochemical functionality and catalytic activity, and therefore there has been a strong desire that the type of compounds be intercalated into the interlayer spaces of the layered metal oxides to form the inorganic–organic nanocomposites with some novel functions. Such intercalation, however, is not easy for most of the organometallic compounds due to their chemical nature and steric hindrance. Thus, so for, only several organometallic-intercalated layered metal oxides have been successfully synthesized [6, 12]. Titanatranes with a formula of $Ti((C_2H_3(R)O)_3N(OR')$ are an important class of chiral titanium(IV) pentacoordinated complexes derived from tetradentate trisalkoxyamine podands. The titanatranes have been widely used in glass industry, manufacture of emulsion paint, and oil extraction, etc. In recent decade, they have been employed as an ideal titanium source for the synthesis of TS-1 zeolite and mesoporous silica containing titanium such as Ti-MCM-48 and Ti-SBA-15 [13]. More interestingly, the pentacoordinated titanatranes were excellent catalysts for the synthesis of cyclic trithiocarbonates from cyclic ethers and carbon disulfide, and the asymmetric oxidation of sulfides to sulfoxides [14–17]. Currently our efforts are aimed at the intercalation of the chiral titanatranes in the interlayer spaces of the layered metal oxides, and the achievement relating to the synthesis process has been briefly presented in a communication form [18]. The intercalated resultants have a potential to be developed as the effective heterogeneous catalysts for these reaction systems. In this paper, we report in detail the intercalation behaviors of titanium(IV) (triethanolaminato)-isopropoxide ($(N(C_2H_4O)_3Ti\text{-}OCH(CH_3)_2$, abbreviated as TEAIP) in different layered protonated metal oxides (HNb_3O_8, $HTiNbO_5$, $HLaNb_2O_7$, $H_2Ti_4O_9$ and $H_2Ti_{2.8}Mn_{0.2}O_7$). Two novel layered nanocomposites, TEAIP-intercalated layered niobic acid and titanoniobic acid obtained from the intercalation reaction between either HNb_3O_8 or $HTiNbO_5$ and TEAIP, have been structurally characterized in detail by employing various measurements such as XRD, FT-IR, TEM, DR-UV–Vis, TG/DTA. In addition, the competitive intercalation between TEAIP and *n*-decylamine in the interlayer space of HNb_3O_8 as well as $HTiNbO_5$ is also investigated.

Experimental

Preparation

The layered protonated transition-metal oxides (HNb_3O_8, $HTiNbO_5$, $HLaNb_2O_7$, $H_2Ti_4O_9$ and $H_2Ti_{2.8}Mn_{0.2}O_7$) were prepared according to literatures [5, 19–22]. The intercalating agent was an isopropyl alcohol solution of TEAIP ($V_{TEAIP}/V_{isopropyl\ alcohol} = 80{:}20$), which was supplied by Aldrich Chemical Company Inc. Before the intercalation experiment, the intercalating agent was further diluted with isopropyl alcohol, forming a solution of $V_{TEAIP}/V_{isopropyl\ alcohol} = 40{:}60$. Each of the layered protonated oxides (2 g) was individually added into 100 mL of the diluted TEAIP solution. After stirring at 313 K for 1 week, the resultant solids were separated by centrifugation, washed with isopropyl alcohol, ethanol and 1:1 aqueous ethanol, and finally dried at ambient temperature. The competitive intercalation of TEAIP and *n*-decylamine in the layered protonated metal oxide was carried out as follows: either HNb_3O_8 or $HTiNbO_5$ (1 g) was mixed with *n*-decylamine (4 mL) and the diluted TEAIP solution (50 mL), followed by continuous stirring for 7 days, and the other procedures including separation, washing and dryness were same as those of resultant of reaction between HNb_3O_8 and TEAIP.

Characterization

Powder XRD patterns were obtained on an ARL-X'TRA diffractometer operating with Cu-K_α radiation and Ni monochromator. Fourier transformation infrared spectra (FT-IR) were recorded on a Nicolet 5DX FT-IR spectrometer using a KBr pellet containing the corresponding sample. Transmission electron micrographs (TEM) were obtained on a JEOL-200CX microscope, which was operated at an accelerated voltage of 200 kV. Thermo-gravimetric and differential thermal analysis (TG/DTA) was carried out with a Netsch STA 449C thermal analysis system at a heating rate of 10 K/min from room temperature to 1,173 K under flowing air. BET (Brunauer–Emmett–Teller) specific surface areas of some calcined samples were measured volumetrically at liquid-nitrogen temperature on a Micromeritics ASAP 2000 apparatus equipped with a computer-controlled measurement system. The samples were degassed by evacuation at 573 K to reach a vacuum below 0.4 Pa before the measurement. UV–Vis diffuse reflectance (DR-UV–Vis) spectra in the range of 200–800 nm were recorded with a Shimadzu

UV-2401 PC spectrometer equipped with a diffuse-reflectance attachment, and with $BaSO_4$ as the reference.

Results and discussion

As the first attempt, we once tried to introduce titanium alkyloxide molecules such as titanium isopropyl oxide and tetrabutyl titanate into the interlayer spaces of the layered metal oxides, but all the experiments were not successful.

The structure and the property of titanatrane TEAIP are different from those of the usual titanium alkyoxides (i.e. $Ti(OR)_4$). As shown in Fig. 1, a TEAIP molecule contains a homochiral trialkanolaminato whose three arms coordinate equivalently to central titanium. The nitrogen atom of $N(C_2H_4O)_3$ group is chelately coordinated to the central titanium. The trialkanolamine(3-) ligand has been reported to possess an ability to stabilize the titanium complex toward hydrolysis in aqueous environments [15].

As shown in Figs. 2 and 3, the basal interlayer distances of HNb_3O_8 and $HTiNbO_5$ are only 1.13 nm (Fig. 1a) and 0.85 nm (Fig. 2a), respectively. After HNb_3O_8 and $HTiNbO_5$ were reacted with the isopropyl alcohol solution of TEAIP, the basal interlayer distance of the former was expanded to 1.56 nm as suggested by the (010) diffraction at $2\theta = 5.7°$ (Fig. 2b) and that of the latter to 1.35 nm as shown by the corresponding (002) diffraction at $2\theta = 6.5°$ (Fig. 3b). The XRD patterns of the as-synthesized products were also indexed as the individual single phase. In order to ascertain whether the intercalated guest molecules were TEAIP or isopropyl alcohol, pure isopropyl alcohol was employed to react with HNb_3O_8 under the same experimental conditions, and the resultant solid was also characterized by XRD. There was no obvious change for the positions of all diffraction peaks after HNb_3O_8 was treated with pure isopropyl alcohol, indicating that the intercalation of the alcohol molecules into the interlayer spaces of the layered solid acids did not occur. Thus, it could be concluded that, when HNb_3O_8 or $HTiNbO_5$ reacted with a solution comprised of TEAIP and isopropyl alcohol, the intercalated guest in the interlayer spaces should be TEAIP, rather than alcohol molecules.

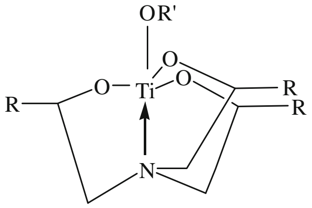

Fig. 1 Structure of titanatranes with a formula of $Ti((C_2H_3(R)O)_3N(OR')$

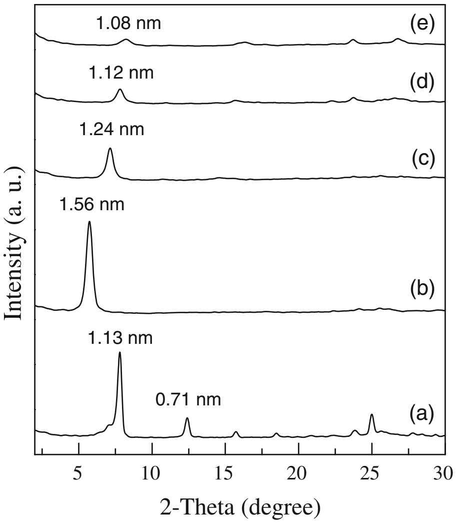

Fig. 2 XRD patterns of (*a*) HNb_3O_8; TEAIP-HNb_3O_8 at (*b*) room temperature; (*c*) 573 K, air, 2 h; (*d*) 673 K, air, 2 h and (*e*) 773 K, air, 2 h

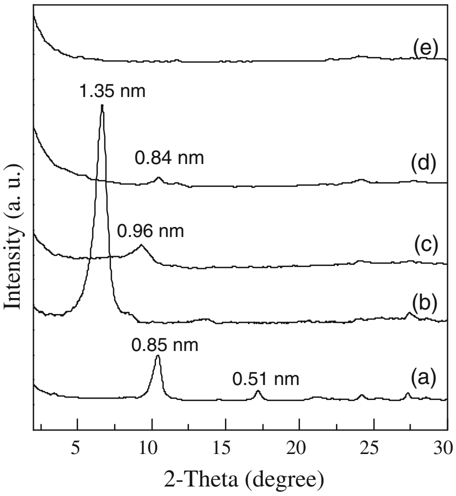

Fig. 3 XRD patterns of (*a*) $HTiNbO_5$; TEAIP-$HTiNbO_5$ at (*b*) room temperature; (*c*) 573 K, air, 2 h; (*d*) 673 K, air, 2 h and (*e*) 773 K, air, 2 h

The FT-IR spectra of the two intercalated products also supported the above conclusion. As seen from Figs. 4a and 5a, both the absorption in the range from ca. 1,065 to 1,100 cm^{-1} and the absorption at ca. 1,150 cm^{-1} are the characteristic absorptions of titanium alkyloxide-like compounds. The former is ascribed to C–O stretching vibration, and the latter is due to C–C stretching vibration [23]. The absorption bands at ca. 1,390 and 1,450 cm^{-1} are ascribed to C–H bending vibration in $-CH_3$ and $-CH_2$, respectively [23]. Those at 1,200–1,260 cm^{-1} may be assigned to C–N vibrations [24]. The interlayer spacings of the TEAIP-intercalated HNb_3O_8 (denoted as TEAIP-HNb_3O_8 hereafter) and $HTiNbO_5$ (denoted as TEAIP-$HTiNbO_5$ hereafter) were

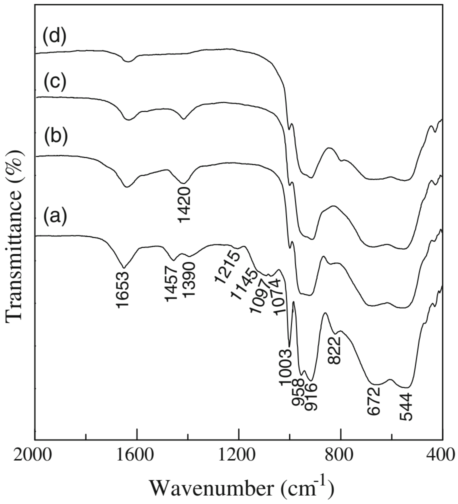

Fig. 4 IR spectra of TEAIP-HNb_3O_8 at (*a*) room temperature; (*b*) 573 K, air, 2 h; (*c*) 673 K, air, 2 h and (*d*) 773 K, air, 2 h

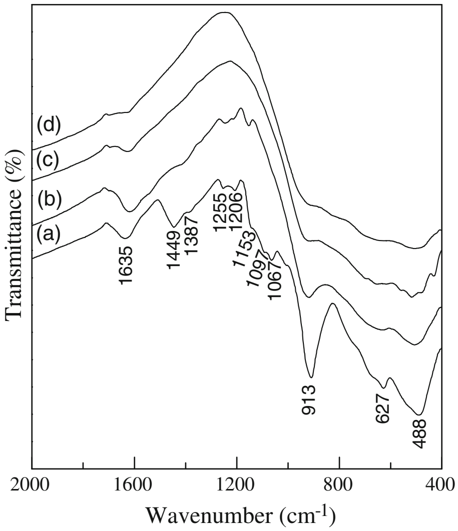

Fig. 5 IR spectra of TEAIP-$HTiNbO_5$ at (*a*) room temperature; (*b*) 573 K, air, 2 h; (*c*) 673 K, air, 2 h and (*d*) 773 K, air, 2 h

evaluated as 0.81 and 0.74 nm, respectively, on the basis of the layer thickness of $Nb_3O_8^-$ (0.75 nm) and $TiNbO_5^-$ (0.61 nm) sheets [25, 26]. The intercalating mechanism may be reasonably considered as follows: when TEAIP molecules penetrated into the interlayer spaces of the layered protonated metal oxides, the chelating coordination of the nitrogen atom to the central titanium disjointed, and the $N(C_2H_4O)_3$ groups incorporated with the interlayered protons, forming $NH(C_2H_4O)_3^+$ ions based on the acid–base reaction.

Transmission electron microscopy (TEM) was used to reveal the texture of the TEAIP-intercalated layered products. The TEM images of TEAIP-HNb_3O_8 and TEAIP-$HTiNbO_5$ are shown in Fig. 6. The well-ordered layered structures of both the nanocomposites are clearly visible.

For the layered nanocomposites, the changing feature of the interlayer distance with temperature can be used to assess their thermostability. As shown in Figs. 2 and 3, upon calcination at 573 K in air, the interlayer distance of TEAIP-HNb_3O_8 decreased from 1.56 nm (Fig. 2b) to 1.24 nm (Fig. 2c) and that of TEAIP-$HTiNbO_5$ rapidly from 1.35 nm (Fig. 3b) to 0.96 nm (Fig. 3c). After heat treatment at 773 K, the (010) diffraction peak of the former was still present (Fig. 2e), but the diffraction peak of the latter fully disappeared (Fig. 3e), indicating that the layered structure of the latter was completely collapsed. This result suggests that the thermostability of TEAIP-HNb_3O_8 would be better than that of TEAIP-$HTiNbO_5$.

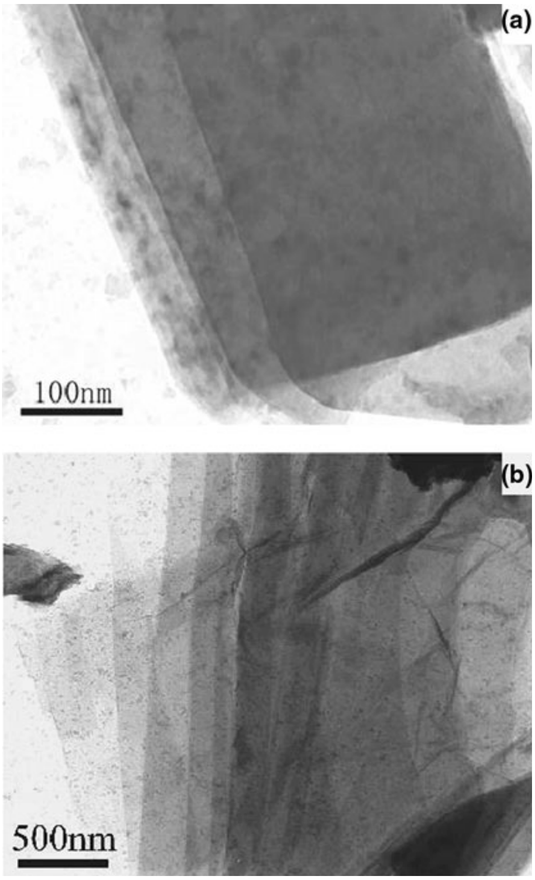

Fig. 6 TEM micrographs of **a** TEAIP-HNb_3O_8 and **b** TEAIP-$HTiNbO_5$

Figure 7 shows UV–Vis spectra of TEAIP-HNb_3O_8 and TEAIP-$HTiNbO_5$. For comparison, the UV–Vis spectra of $Ti((C_2H_4)O)_3N(OiPr')$, HNb_3O_8 and $HTiNbO_5$ are also given in this figure. $Ti((C_2H_4)O)_3N(OiPr')$ had a absorption band extending from 200 to 400 nm, in which the maximum absorption appeared in around 320 nm. This spectral feature is due to the charge transfers between the O^{2-} ligand and the titanium(IV) ion. Both HNb_3O_8 and $HTiNbO_5$ exhibited an absorption band with an absorption

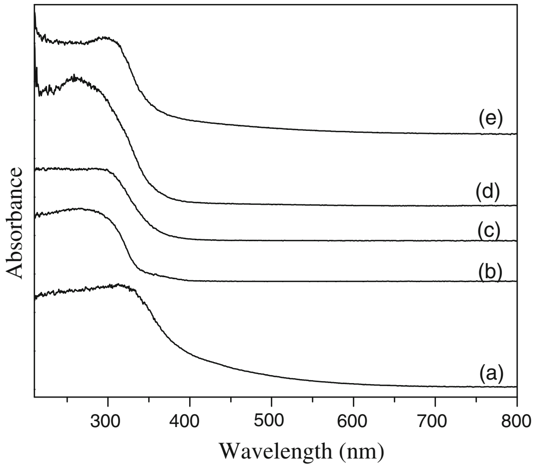

Fig. 7 DR-UV–Vis spectra of (*a*) $Ti((C_2H_4(R)O)_3N(OR'))$, (*b*) HNb_3O_8, (*c*) $HTiNbO_5$, (*d*) TEAIP-HNb_3O_8 and (*e*) TEAIP-$HTiNbO_5$

edge at about 350 and 370 nm, respectively. Such features may be assigned to a charge transfer excitation within MO_6 (M = Nb or Ti) octahedral units in the sheet framework. Compared respectively with HNb_3O_8 and $HTiNbO_5$, although the absorption edges of TEAIP-HNb_3O_8 (Fig. 7d) and TEAIP-$HTiNbO_5$ (Fig. 7e) had no significant change, the two novel nanocomposites exhibited the maximum absorption around 260 and 300 nm, respectively, indicating that there were an interaction between the TEAIP molecules and the host sheets. This is also a collateral evidence for the intercalation of TEAIP guest in interlayers of the layered hosts.

TG-DTA curves of the two nanocomposites are illustrated in Fig. 8. The first main weight-loss step below ca. 523 K for both materials is assigned to the loss of water adsorbed on the surface and in the interlayers, and those from ca. 523 to 823 K for TEAIP-HNb_3O_8 and from ca. 523 to 753 K for TEAIP-$HTiNbO_5$ are attributed to the oxidative decomposition of the intercalated TEAIP molecules. Interestingly, two weight-loss steps are observed for TEAIP-HNb_3O_8 in the range of 523–823 K, but only one weight-loss step for TEAIP-$HTiNbO_5$ in the corresponding temperature range of 523–753 K. This may be due to the structural and acidic difference of the two layer hosts. The weight loss from 753 to 1,073 K in TG curve of TEAIP-$HTiNbO_5$ is assigned to the dehydration of the $HTiNbO_5$ host, during which the layered structure collapses. The TG-DTA profiles of TEAIP-HNb_3O_8 also suggest that an intermediate with a relatively high heat-resistant quality was formed when the intercalated TEAIP molecules decomposed in air. The conclusion drawn from TG-DTA profiles is also supported by FT-IR result. As shown in Fig. 4b, when TEAIP-HNb_3O_8 was calcined at 573 K, a new absorption peak at ca. 1,420 cm^{-1} appeared, and this peak was still retained upon calcination at 673 K. Based on the TG curves of the two nanocomposites, the amounts of the guest TEAIP intercalated into the interlayer spaces were estimated to be 0.17 and 0.14 mol per mol of HNb_3O_8 and $HTiNbO_5$, respectively, indicating that the protons in the interlayers were not completely replaced by TEAIP molecules. This result is ascribed to the great steric hindrance of the guest molecules. Based on this fact, we infer that there should be a good deal of vacant space in the interlayers of TEAIP-HNb_3O_8 as well as TEAIP-$HTiNbO_5$. Such structural feature would be convenient to accommodate organic molecules and accordingly is advantageous to catalytic reaction such as the asymmetric oxidation of sulfides to sulfoxides and the catalytic synthesis of cyclic trithiocarbonates from cyclic ethers and carbon disulfide. Nugent and Harlow [15] pointed out that the chelating (tetradentate) chiral alkoxide ligands, namely, trialkanolamines, could stabilize titanium alkoxides toward hydrolysis in aqueous environments; and that this would be a highly asymmetric environment in the vicinity of the transition metal. Wang et al. [27] reported that there was a weak bond between N and Ti. Here, it could be reasonably speculated that when HNb_3O_8 or $HTiNbO_5$ reacted with a solution comprised of TEAIP and isopropyl alcohol, the

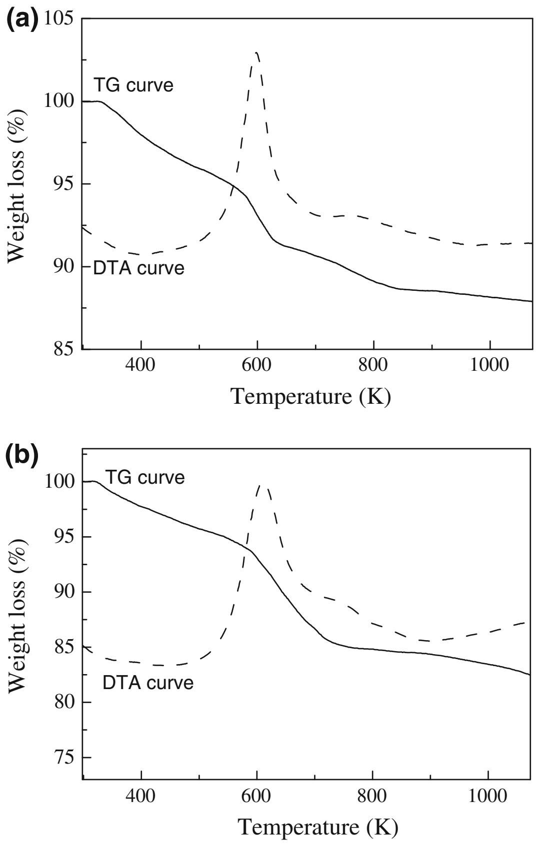

Fig. 8 TG-DTA curves of **a** TEAIP-HNb_3O_8 and **b** TEAIP-$HTiNbO_5$

weak N–Ti bond broke, but the basic structure of titanium alkoxides possessing highly asymmetric environment was unchanged. According to the compositions of the intercalation compounds (TEAIP-HNb_3O_8 and TEAIP-$HTiNbO_5$) quantitatively estimated from the TG-DTA data, the chemical formulas of the TEAIP-HNb_3O_8 and TEAIP-$HTiNbO_5$ can be expressed as $(TEAIP)_{0.17}H_{0.83}Nb_3O_8$ and $(TEAIP)_{0.14}H_{0.86}TiNbO_5$, respectively.

From FT-IR spectra shown in Figs. 4d and 5c, it can be concluded that the intercalated TEAIP molecules were completely decomposed at 773 K in the case of TEAIP-HNb_3O_8 and at 673 K in TEAIP-$HTiNbO_5$. Since at this time both the calcined samples still exhibited layered structures, as seen in Figs. 2e and 3d, thus the titania particles formed during the decomposition processes remained in the interlayer spaces. The BET specific surface areas of the calcined samples were determined to be 29.2 and 25.6 $m^2\ g^{-1}$, respectively, which were obviously higher than those of the corresponding starting materials (S_{BET} of HNb_3O_8: 6.8 $m^2\ g^{-1}$; S_{BET} of $HTiNbO_5$: 3.8 $m^2\ g^{-1}$).

The acid–base intercalation reaction between the layered $H_2Ti_4O_9$ and the TEAIP guest was not found to occur, and the corresponding XRD result is not presented in this paper. The behavior of $H_2Ti_{2.8}Mn_{0.2}O_7$ was similar to that of $H_2Ti_4O_9$. The acid–base intercalation reaction between the layered $HLaNb_2O_7$ and the TEAIP guest did occur, though this intercalation was incomplete. As shown in Fig. 9, after $HLaNb_2O_7$ was treated with the alcohol solution of TEAIP, a new diffraction peak at $2\theta = 5.4°$ appeared, but the peaks at $2\theta = 8.1°$, 22.8°and 28.4° corresponding to the characteristic diffractions of $HLaNb_2O_7$ did not disappear. That was, there were two phases in resultant product of reaction between $HLaNb_2O_7$ and TEAIP. The new peak arose from the partially intercalation of TEAIP molecules in the interlayer spaces of $HLaNb_2O_7$. This intercalation resulted in an expansion of the interlayer distance from 1.09 to 1.65 nm (Fig. 9b). Obviously the new peak is relatively weak in comparison with (001) diffraction of $HLaNb_2O_7$, revealing that the intercalation in this case should be rather difficult.

Since the intercalation mechanism is based on acid–based reaction, the different intercalation behavior of TEAIP in HNb_3O_8, $HTiNbO_5$, $HLaNb_2O_7$, $H_2Ti_4O_9$ may be explained by the difference of these layered protonated oxides in acidity. Among the layered protonated oxides, the acidity of HNb_3O_8 and $HTiNbO_5$ is relatively strong, and that of $H_2Ti_4O_9$ is low [28, 29]. On the other hand, it is well known that the layer charge density of the matrices has also an important effect on the intercalation of the guest. As seen from the structures of the corresponding layered transition metal oxides (KNb_3O_8, $KTiNbO_5$, $KLaNb_2O_7$ and $K_2Ti_4O_9$) [1], the charge density of $Nb_3O_8^-$ sheet is highest, that of $Ti_4O_9^{2-}$ lowest, and that of $KTiNbO_5$ or $KLaNb_2O_7$ falls in between.

The competitive intercalation of *n*-decylamine and TEAIP in the interlayer spaces of HNb_3O_8 was examined by XRD. After the competitive reaction, as shown in Fig. 10b, the characteristic diffraction peaks of HNb_3O_8 fully disappeared, while three new peaks appeared. Among these peaks, the one at $2\theta = 5.7°$ corresponds to the characteristic (010) diffraction of TEAIP-intercalated HNb_3O_8 as observed in Fig. 2b, while the two others at $2\theta = 3.3°$and 6.5° as observed in Fig. 10a, are indexed to the (010) and (020) diffraction of *n*-decylamine-intercalated HNb_3O_8, respectively.

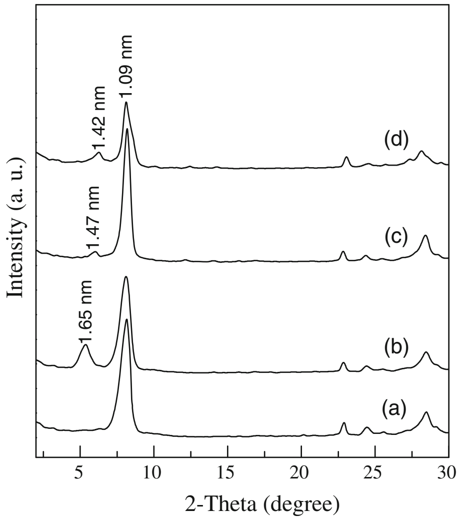

Fig. 9 XRD patterns of (*a*) $HLaNb_2O_7$; TEAIP-$HLaNb_2O_7$ at (*b*) room temperature; (*c*) 573 K, air, 2 h and (*d*) 673 K, air, 2 h

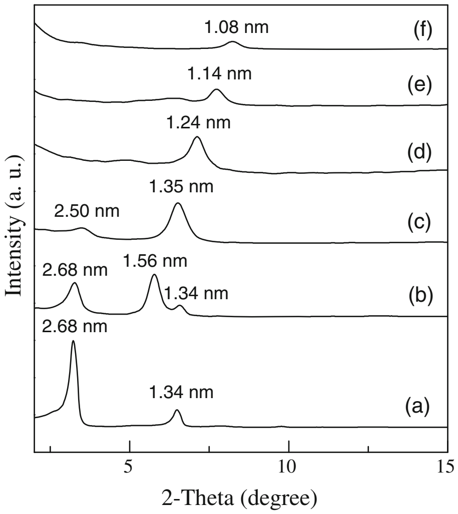

Fig. 10 XRD patterns of (*a*) *n*-decylamine-intercalated HNb_3O_8 and the competitive intercalation product at (*b*) room temperature; (*c*) 473 K air, 2 h; (*d*) 573 K, air, 2 h; (*e*) 673 K, air, 2 h and (*f*) 773 K, air, 2 h

The thermostability of the two intercalated phases was further investigated. The *n*-decylamine-intercalated phase was thermally unstable compared with the TEAIP-intercalated phase, as shown in Fig. 10c–f. The characteristic (010) and (020) diffraction peaks of the *n*-decylamine-intercalated phase nearly disappeared upon calcination at 573 K, while the (010) diffraction peak of the TEAIP-intercalated phase was still maintained up to 773 K, although there was a gradually shift of the peak toward high 2θ angle. The difference between the two intercalated phases in thermostability is mainly related to the difference of the two corresponding guest molecules in thermostability.

It should be pointed out that the competitive-intercalation behavior of the two guests in $HTiNbO_5$ was different from that in HNb_3O_8. When $HTiNbO_5$ was mixed with *n*-decylamine and TEAIP together, only *n*-decylamine-intercalated phase could be finally formed. This result, together with the competitive-intercalation result of *n*-decylamine and TEAIP in HNb_3O_8, can be reasonably interpreted by the relatively weak acidity of $HTiNbO_5$ compared with HNb_3O_8, and the relatively weak basicity and relatively great steric hindrance of TEAIP compared with *n*-decylamine.

Concluding remarks

TEAIP can be intercalated into the interlayer spaces of layered HNb_3O_8 as well as $HTiNbO_5$ via the acid-base reaction mechanism, and as a result, two novel inorganic–organic hybrid nanocomposites, $(TEAIP)_{0.17}H_{0.83}Nb_3O_8$ and $(TEAIP)_{0.14}H_{0.86}TiNbO_5$, have been successfully obtained. This achievement is the first example that organo-titanium compound has been incorporated in the layered metal oxide host. Since TEAIP is a chiral guest, the novel inorganic–organic hybrid materials have a potential to be developed as the heterogeneous chiral catalysts for some chemical processes involving liquid-state organic compounds, such as asymmetric oxidation of organic sulfides. It is well known that the use of heterogeneous catalysts may avoid the trouble that the catalyst is separated from the corresponding reaction system. Such trouble is often suffered in homogeneous catalysis. Neither $H_2Ti_4O_9$ nor $H_2Ti_{2.8}Mn_{0.2}O_7$ reacts with TEAIP to form any intercalated phase. $HLaNb_2O_7$ can only accommodate a limited amount of the guest molecules, forming a partially intercalated phase with TEAIP. The competitive intercalation results show that both TEAIP and *n*-decylamine can be intercalated at the same time in HNb_3O_8 to form two individual intercalated phases, while only *n*-decylamine is intercalated in $HTiNbO_5$. The different acidity of layered hosts, and different basicity and steric hindrance of guest molecules can be used to explain the obtained results. The present research work expands the scope of intercalated layered metal oxides and inorganic–organic hybrid nanocomposites. It can be expected that some other chiral titanatranes ($N(CH_2CH(R)O)_3Ti(OR')$) with specific functional groups R and R′ will be successfully intercalated into the interlayer spaces of layered metal oxides in the near future. Doubtlessly, the catalytic performances of the two novel compounds in some asymmetric oxidation reactions and the related characterization aiming at the heterogeneous catalysts such as BET specific surface area and porous structure are also significant work for the future.

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