Synthesis of silica-pillared layered titanium niobium oxide

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A silica-pillared layered titanium niobium oxide with high thermal stability has been synthesized and characterized for the first time.

The successful methods for preparation of pillared materials that were first developed from pillaring clays and clay minerals,[1–3] led to many attempts to prepare new classes of porous materials, which can be used as shape-selective catalysts and molecular sieves.[4,5] There are also a wide variety of layered metal oxides that have the potential to undergo ion-exchange reactions similarly to clays, but the pillaring procedures developed for smectite clays are not generally applicable to these laminar metal oxides that do not spontaneously delaminate in aqueous media owing to their high charge densities on the frameworks. Recently, the preparation of alumina-pillared layered sodium trititanate, $Na_2Ti_3O_7$[6] and silica-pillared layered tetratitanate $K_2Ti_4O_9$[7] have been reproted. Silica is one of the most commonly used pillars. Silica-pillared layered lanthanum–niobium oxides were also prepared and investigated as catalysts.[8,9] As for titanium–niobium oxides, Wadsley[10] first prepared potassium titanoniobate $KTiNbO_5$ and found that it had a layered structure. Raveau and coworkers[11–13] studied the ion-exchange properties of potassium titanoniobate $KTiNbO_5$ and the intercalation of organic materials into titanoniobic acid. Nakato *et al.*[14] reported the preparation of a methyl viologen–$HTiNbO_5$ intercalation compound. We report here the preparation of silica-pillared layered titanoniobate with high porosity and good thermal stability by a novel pillaring method, in which *n*-hexylamine and tetraethylorthosilicate [$Si(OEt)_4$] are employed as an interlayer exchange guest and a pillar precursor, respectively.

The starting material, layered potassium titanoniobate $KTiNbO_5$ was prepared by heating a mixture of K_2CO_3 (Katayama), TiO_2 (Katayama) and Nb_2O_5 (Wako) (molar ratio = 1 : 2 : 1) at 1060 °C in air. Ion exchange of $KTiNbO_5$ was carried out with 6 M HNO_3 at room temperature for 72 h to afford $HTiNbO_5$. Since $HTiNbO_5$ cannot react directly with tetraethylorthosilicate to form an intercalate, the *n*-hexylamine–$HTiNbO_5$ intercalation compound was prepared first in order to increase the interlayer distance and lower the charge density.

n-Hexylamine-intercalated titanoniobate was obtained by adding $HTiNbO_5$ to a 50% *n*-hexylamine (Wako)–ethanol (Wako) solution and stirring at room temperature for one week, followed by filtering off the product and washing successively with ethanol–water (1 : 1) and distilled water. The obtained *n*-hexylamine-intercalated titanoniobate (3.0 g) was then added to 120 ml of tetraethylorthosilicate (Wako). Having failed to obtain a silica-pillared titanoniobate by reaction between *n*-hexylamine-intercalated titanoniobate and tetraethylorthosilicate at room temperature, the present operation was performed by stirring for one week at *ca.* 65 °C with two additions of tetraethylorthosilicate (40 ml) during this period. After the reaction, the product was separated and washed as above and finally dried at room temperature. Obtained products were studied by X-ray diffraction (Gigaku Geigerflex, Cu-Kα radiation). In $KTiNbO_5$, units consisting of two MO_6 (M = Ti, Nb) octahedra are linked in the *b*-direction to form layers with the potassium ions in the interlayer spaces. XRD analysis shows [Fig. 1(*a*), 2(*b*)] that obtained $KTiNbO_5$ has an interlayer distance of 9.01 Å by measuring the first diffraction peak (2θ = 9.82°) which decreases to 8.28 Å (2θ = 10.69°) upon exchanging K^+ with H^+ in HNO_3 solution, which is comparable to the value of 8.35 Å[11] but is smaller than 8.5 Å[4] published previously. These differences may be due to the differential preparation conditions. As shown in Fig. 1(*c*), *n*-hexylamine readily intercalates layered titanoniobate and leads to an extremely strong peak at 2θ = 4.08 Å. This interlayer distance is 21.7 Å, which is more than twice that of $HTiNbO_5$. The *n*-hexylamine intercalated titanoniobate had rather low thermal stability, and collapses after calcination at 400 °C [Fig. 1(*d*)]. However, the opened layers can facilitate the reaction of layered-hexylamine intercalated titanoniobate with tetraethylorthosilicate, which gives rise to a lower 2θ (3.68°) and a larger layer distance [24.01 Å, Fig. 1(*e*)]. Fig. 1(*f*) shows that the interlayer distance of the product calcined at 400 °C decreases remarkably to 15.61 Å (2θ = 5.66°) as a result of decomposition of organic matter. The peak is still retained upon heat treatment at 600 °C with only slightly increased 2θ and lower intensity [Fig. 1(*h*)]. TG–DTA analysis at a heating rate of 5 °C min^{-1} for the product intercalated with tetraethylorthosilicate indicated that the interlayer organic matter was decomposed between 300 and 440 °C, and no mass loss was observed at higher temperatures. From these results, it is concluded that silica-like clusters are formed in the interlayer, which act as pilalrs to prop up the titanoniobate layers after interlayer

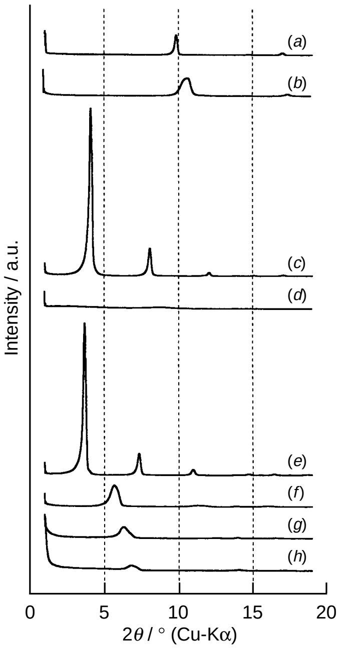

Fig. 1 Cu-Kα X-ray diffraction patterns of (*a*) $KTiNbO_5$ synthesized at 1060 °C; (*b*) as (*a*), proton-exchanged by 6 M HNO_3 at room temperature for 72 h; (*c*) reaction product of $HTiNbO_5$ with *n*-hexylamine solution; (*d*) as (*c*), calcined in air at 400 °C for 2 h; (*e*) reaction product of *n*-hexylamine-intercalated titanoniobate with tetraethylorthosilicate; (*f*) as (*e*), calcined in air at 400 °C for 2 h; (*g*) as (*f*), calcined in air at 500 °C for 2 h; (*h*) as (*g*), calcined in air at 600 °C for 2 h.

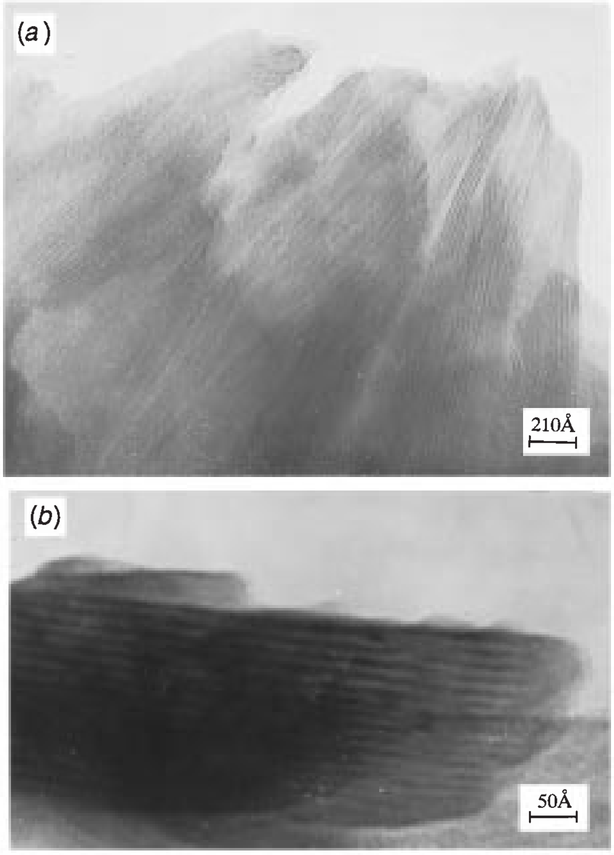

Fig. 2 TEM image of layered silica-pillared titanium niobium oxide with no calcination (*a*) and calcined at 500 °C for 2 h (*b*)

organic matter is removed. The interlayer spacing of the product calcined at 500 °C is found to be 14.05 Å [$2\theta = 6.29°$, Fig. 1(*g*)], which is nearly twice that of $HTiNbO_5$. Fig. 2 shows transmission electron microscopy (TEM, recorded with a JEOL JEM-200CX microscope) images of untreated silica-pillared layered titanoniobate [Fig. 2(*a*)] and a sample calcined at 500 °C [Fig. 2(*b*)]. The layer structures are clearly visible, and the interlayer separations observed by TEM are consistent with those obtained from XRD. While the interlayer spacing of the material increases, the BET surface area of the titanoniobates increases from 1.8 $m^2 g^{-1}$ for the original $KTiNbO_5$ to 20.0 $m^2 g^{-1}$ for pillared SiO_2–$TiNbO_5$ calcined at 500 °C, and decreases to 11.3 $m^2 g^{-1}$ at 600 °C. Elemental analysis results showed that the SiO_2 content in this silica-pillared material is *ca*. 56 mass%. The BET surface area is perhaps lower than expected due to a large amount of SiO_2 incorporated into the interlayers and the weak Bronsted acidity of $HTiNbO_5$ as compared to some layered compounds.[15]

The UV–VIS spectra of SiO_2–$TiNbO_5$ shifted into the visible region as compared to those of $KTiNbO_5$ and $HTiNbO_5$. Hydrogen evolution from the photocatalytic decomposition of water on the pillared layered titanoniobate was observed under a mercury lamp and sunlight. Thus, the new material is expected to show photocatalytic activity. Future investigation on its systematic characterization and catalytic properties is being undertaken.

Notes and References

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