Local structure analysis of Ti species stabilized in ion exchangeable layer solids by x-ray absorption spectroscopy

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Nano-sized titanium dioxides are incorporated into the interlayer spaces of ion-exchangeable layered perovskites, $H_{1-x}Ca_{2-x}La_xNb_3O_{10}$ (x=0.0~0.75), by replacing the interlayer protons with positively charged TiO_2 nano-sol particles or basic titanium glycolate complex (titanatrane). Powder X-ray diffraction analysis, UV-Vis absorption spectroscopy, thermogravimetric analysis, and N_2 adsorption-desorption isotherm measurements show that quantum sized TiO_2 particles are stabilized inbetween perovskite lattices to form micropores (S_{BET}= 37~110 m^2/g). X-ray absorption spectroscopy at the Ti K-edge was used for investigating the local environment around Ti atoms constituting the interlayer pillars. According to the XANES spectra, the ‘as-pillared’ Ti species have the same local environments with those of precursory species, which subsequently converted into TiO_2 clusters with rutile and anatase-like local structures when TiO_2 nano–sol particles and titanatrane are used as pillaring species, respectively. It is also found that the local environment of TiO_2 remains almost constant irrespective of the layer charge density, while the TiO_2 pillar content and the microporosity increase with the latter.

Keywords: layer perovskite, nanoparticle, titanium dioxide, pillaring, microporosity, XANES.

1. Introduction

Layer metal oxides such as layered titanates and niobates are typical wide band gap semiconductive oxides, which can produce photoelectrons and holes under UV irradiation and are of special interest because of their possible applications to conversion of solar energy into chemical energy and to detoxification of hazardous organics under UV irradiation (Domen *et al.*, 1996; Ebina *et al.*, 1996; Yanagisawa *et al.*, 1998). In particular, the layered titanates and niobates, including $K_2Ti_4O_9$, $KTiNbO_5$, $K_4Nb_6O_{17}$, $KCa_2Nb_3O_{10}$, etc., possess ion exchangeable interlayer cations, which can be easily replaced by foreign organic and inorganic species, offering a way to modify the interlayer environments and their catalytic properties. Thus, to achieve high efficiency in energy conversion and photocatalytic activity of the layered metal oxides, much efforts have been made to the exploitation of the interlayer spaces using ion exchange, pillaring, and exfoliation processes (Domen *et al.*, 1996; Abe *et al.*, 1998; Sasaki *et al.*, 1997). In the view point of photocatalysts, pillaring of semiconductor particles with different energy level between the semiconductive oxide layers offers a promising way to achieve the efficient hole (h^+)-electron (e^-) charge separation by retarding the charge recombination. Furthermore pillaring of semiconductive oxides into the oxide layers gives rise to the creation of many voids, that is nanopores, between the pillars and oxide layers, leading to increase in specific surface area and porosity, and photocatalytic activity.

In general, semiconductor pillars are constructed by the intercalation of soluble inorganic species, followed by the conversion of the interlayered species into robust metal oxides by chemical, thermal and/or photochemical reactions. By using TiO_2 sols, TiO_2 pillars were successfully constructed in clay minerals that swell in water largely (Yoneyama *et al.*, 1989). However, it is not easy to introduce TiO_2 pillars in semiconductive layer compounds such as titanates and niobates, since they do not swell in water probably due to the high charge density of the metal oxide layers. In the present study, therefore, to facilitate the incorporation of TiO_2 species inbetween perovskite slabs, the interlayer charge density is reduced by replacing some of the Ca^{2+} ions with La^{3+} ions, $K_{1-x}Ca_{2-x}La_xNb_3O_{10}$. Furthermore, the rigid oxide layers are expanded with octylammonium molecules prior to the intercalation of Ti-species in order to provide an initially greatly expanded gallery space. In particular, the present study focuses on the elucidation of the local environments and electronic structures of Ti-species stabilized in the perovskite-like layers using X-ray absorption spectroscopy.

2. Experimentals

2.1 Sample preparation

A series of $K_{1-x}Ca_{2-x}La_xNb_3O_{10}$ (x=0.00, 0.25, 0.50, and 0.75) was prepared by reacting appropriate quantities of K_2CO_3, La_2O_3, $CaCO_3$, and Nb_2O_5 at 1000 °C ~ 1200 °C for 48 h with one grinding inbetween. Excess (10 mol%) of K_2CO_3 was added to compensate for the loss due to volatilization. Thus prepared K-forms were converted into H^+-derivatives by refluxing the solids in 4N-HCl at room temperature for 24 h under continuous stirring. The interlayer protons were further replaced by octylammonium cations ($n\text{-}C_8H_{17}NH_3^+$) to expand the perovskite slabs. Typically, 1g of proton derivative was reacted with 5 ml octylammine in ethanol solution (10 ml) for 24 h. The reaction products were separated by centrifugation, washed with distilled water several times and dried under vacuum.

A TiO_2 nano-sol solution was prepared by the hydrolysis of titanium tetraisopropoxide, $Ti(OC_3H_7)_4$, with 1N-HCl so as to give a final molar ratio of 0.25 of the alkoxide to HCl (Yoneyama *et al.*, 1989). The resulting slurry was peptized by further stirring for 3 h at room temperature to give a clear titania sol. As a novel pillaring precursor of titanium, a basic titanatrane glycolate complex prepared by the reaction of TiO_2, ethanolamine ($N(CH_2CH_2OH)_3$) and ethylene glycol was also applied for the first time in the TiO_2 pillaring reaction. In the pillaring of TiO_2 sol particle, octylammonium derivatives were mixed with TiO_2 sol solution with a mole ratio of Ti to x in the $(C_8H_{17}NH_3^+)_xCa_{2-x}La_xNb_3O_{10}$ to 30. After being reacted at room temperature for 15 h, the samples were separated by centrifugation, washed with a mixed solution of water and ethanol (1:1 vol. ratio), and dried in air. Finally, the TiO_2 pillars were constructed by thermal reaction at 200 °C for 4 h under vacuum oven. In the pillaring reaction using titanatrane glycolate complex, the proton-derivatives were directly reacted with titanatrane complex (titanatrane/x = 5 in mole) in ethanolic solution at 80°C for 2 days. Similarly, the reaction products were separated by centrifugation, washed with ethanol solution thoroughly, and dried under vacuum. Then the interlayered titanatrane complex was converted into TiO_2 by thermal reaction at 550 °C for 3 h under an ambient atmosphere.

2.2 Sample characterization

The crystalline phases of the reaction products were identified with power X-ray diffraction analysis (MacScience MXP3) using Ni-filtered Cu-Kα radiation (λ=1.54184 Å). The specimens for XRD measurement were prepared by spreading the wet-samples on slide glasses to make preferred orientation. Thermogravimetric (TG) and differential thermal analysis (DTA) was performed on a Seiko TG/DTA320 instrument under ambient atmosphere. Diffuse-reflectance UV-Vis spectra were recorded on a UV-VIS-NIR spectrophotometer, CARY 5G. The specific surface areas were determined from the nitrogen adsorption-desorption isotherms with a Sorptomatic 1990 (CE Instruments). All the samples were degassed by evacuation at 250 ºC for 5 h under reduced pressure (< 1 torr) prior to sorption measurements. Field-emission scanning electron microscopy (FE-SEM) was carried out with a HITACHI S-4200 electron microscope, operating at 30 kV.

The Ti K-edge X-ray absorption spectra were recorded at beamline EXAFS3C1 at the Pohang Accelerator Laboratory (PAL), operated at 2.5 GeV with *ca.* 100 ~ 150 mA of stored current. A Si (311) double crystal monochromator was employed to collect high resolution XANES spectra. The absorption energy was calibrated using Ti-metal foil (E_o=4964.2 eV). The XANES data for the TiO_2 sol pillared samples were recorded in transmission mode while for the titanatrane intercalated ones were collected in fluorescence mode using a Lytle detector. The XANES spectra were processed according to the following procedure using the program WinXAS: the spectra were normalized in absorbance by fitting the spectral region from 4850 to 4950eV (the region before the pre-edge) using a first-order polynomial function and subtracting this as background absorption. Thereafter, the edge jump was normalized to a value of 1 for the absorption, based on the linear variation of the average absorption coefficient of the spectral region from 5050 to 5200eV.

3. Results and discussion

Fig.1 shows the evolution of powder X-ray diffraction patterns for the samples obtained at the various stage of pillaring reaction. The pristine $HCa_2Nb_3O_{10}$ (a) exhibits a series of (*00l*) reflections with a basal spacing of 14.3 Å. Upon intercalation of octylammonium cations into the perovskite slabs, the basal spacing expands up to ~ 34 Å irrespective of the interlayer charge density of x. Assuming that the thickness of perovskite slab itself, $Ca_2Nb_3O_{10}^-$, is ~ 11.5 Å and the theoretical molecular length of octylammonium (OA) cation is 11.5 Å (Galarneau *et al.*, 1995), the interlayered alkylammonium molecules adopt paraffin-like bilayer arrangement. Subsequent reaction of the OA-derivative with the TiO_2 sol solution leads to the decrease of the basal spacing to ~ 23 Å (c), indicating that the interlayered alkylammonium cations are replaced by the positively charged TiO_2 nano-sol particles. The basal spacing is further reduced to ~ 16 Å after thermal treating at 200°C for 4 h (d) due to the contraction of pillar species.

The reaction between titanatrane glycolate complex and $HCa_2Nb_3O_{10}$ gives rise to an increase of basal spacing from 14.3 Å to 22.1 Å, indicating the successful intercalation of the Ti-complex into the interlayer space of the layer niobate (e). A direct acid-base reaction between the interlayer protons and the titanatrane glycolate complex may be responsible for the intercalation reaction. Upon heating the titanatrane-intercalated sample at 550 °C for 3 h to remove the organic residue leads to the decrease of the basal spacing to 14.1 Å (f). The gallery height due to the pillaring of TiO_2 is estimated to be 2.6 Å, which is smaller than that of the TiO_2 sol pillared one (~ 4.5 Å). It is worthy to note here that the basal spacings of the modified samples are almost constant irrespective of the interlayer charge density of the pristine $H_xCa_{2-x}La_xNb_3O_{10}$. This reflects that the interlayer separation is mainly governed by the dimension of gallery species not by the incorporated amount.

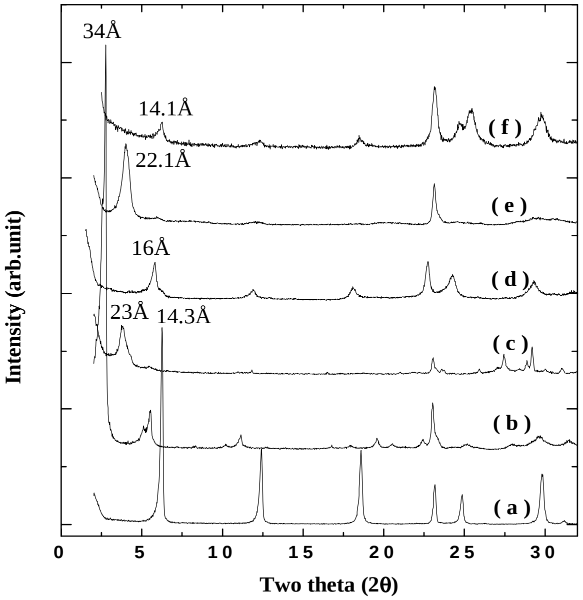

Figure 1
Powder X-ray diffraction patterns of the (a) pristine $HCa_2Nb_3O_{10}$, (b) octylammonium intercalated $Ca_2Nb_3O_{10}$, (c) TiO_2-sol exchanged $Ca_2Nb_3O_{10}$, (d) heat-treated the sample (c) at 200°C for 4h, (e) titanatrane intercalated $Ca_2Nb_3O_{10}$, and (f) heat-treated the sample (e) at 550°C for 3h.

The specific surface area of the pristine $HCa_2Nb_3O_{10}$ (S_{BET} = ~ 2m^2/g) is largely increased upon pillaring with TiO_2 sol particles to 37 ~ 110 m^2/g, indicating the creation of interlayer pores between pillars and perovskite layers. Here the BET specific surface area of the pillared samples shows a strong correlation with the interlayer charge density (x); specific surface area increases as the x decreases. This result is not surprising given the high layer charge of the perovskites. As the interlayer charge density is higher, TiO_2 pillar density in the unit area is larger, stuffing the interlamellar spaces with pillar species and consequently lowering the free space between the oxide layers.

X-ray absorption spectroscopic measurement at the Ti K-edge was carried out in order to obtain structural information on the titanium species stabilized in the interlayer space of the layered perovskite. Fig.2 represents the XANES spectra of TiO_2 sol exchanged calcium niobate system measured in transmission mode. Comparing the pre-edge and main edge features reveals that TiO_2 species stabilized between the interlamellar spaces (c-f) have the same structural character as the precursor TiO_2 sol solution (b), indicating the successful intercalation of TiO_2 sol particles into the interlayer spaces of the perovskites. In addition, the local structure of the interlayered TiO_2 species are constant irrespective of the interlayer charge density. Taking into account the XRD result, TiO_2 clusters with the size of ~ 4.5 Å are expected to be stabilized between the layers. The three small pre-edge peaks of the pillared samples, which are assigned to transition for the 1s core level of Ti to 3d orbitals, suggesting that the titanium atoms in the interlayer pillars occupies sites of octahedral symmetry. The relative intensities of these pre-edge features can be a sensitive measure of the local coordination environment around the central absorbing Ti atom. The XANES features for the pillared samples well consistent with that of rutile-type TiO_2 (Joly *et al.*, 1999) rather than anatase-type TiO_2 (a), indicating that the precursory TiO_2 nano-sol particles have already rutile-like local structure even before pillaring reaction.

Fig.3 shows the XANES spectra of the TiO_2 pillared calcium niobate system using the titanatrane complex recorded in fluorescence mode. When the titanatrane glycolate is used as a pillaring species, the concentration of Ti in the interlamellar region is very low due to the high charge-to-molecule ratio of titanatrane compared with that of TiO_2 sol particle. Thus the fluorescence technique was applied to obtain good XANES spectra with high S/N ratio. Comparing the spectra of titanatrane glycolate (b) and its layer hybrid (c) reveals that the Ti-complex is successfully incorporated into the interlamellar space of layer perovskite with preserving the structural integrity. An enlargement of the pre-edge region is shown in the inset where three different features labelled A1, A2, and A3 can be distinguished. A detailed assignment of electronic transition to these features is performed in accordance to the literature (Joly *et al.*, 1999). Feature A1 is only quadrupolar t_{2g}; A2 is dipolar in nature but includes also a little e_g quadrupolar component. ; A3 is a pure dipolar feature. Upon calcining the titanatrane intercalated niobate at 550 °C (d), the pre-edge feature becomes close to that of the anatase-type TiO_2 (a). It is worthy to note here that the interlayer titanatrane complex is converted into the anatase-type TiO_2 whereas the pillaring of TiO_2 sol particle leads to the rutile-type TiO_2. The lower Ti content in the titanatrane compared with that of TiO_2 sol particles and the spatial confinement would be responsible for the stabilization of anatase-type TiO_2 in the interlayer spaces of layered perovskite.

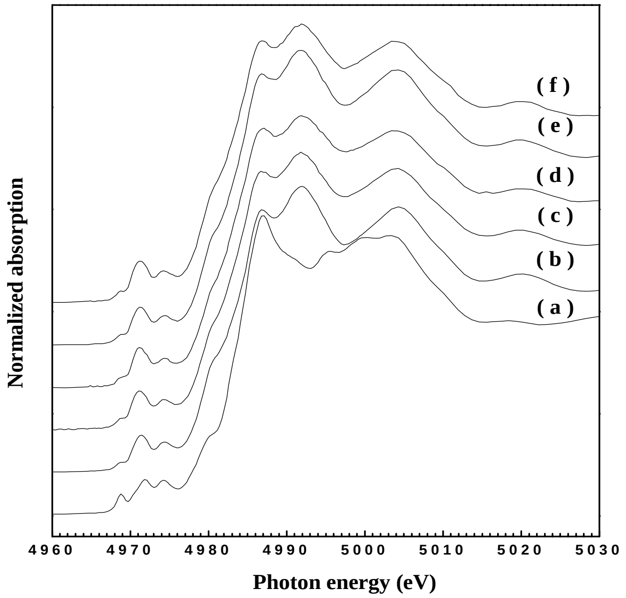

Figure 2
Ti K-edge XANES of the TiO_2 pillared calcium niobates measured in transmission mode; (a) anatase (reference), (b) TiO_2 sol solution, (c) x=0.0, (d) x=0.25, (e) x=0.50, and (f) x=0.75.

4. Conclusions

Nanocrystalline TiO_2 semiconductors are successfully stabilized in the interlayer space of layer perovskite, $H_{1-x}Ca_{2-x}La_xNb_3O_{10}$ by a guest-exchange reaction between octylammonium cation and positively charged TiO_2 sol particle and a direct acid-base reaction between interlayer proton and titanatrane glycolate complex. It is found that the reduction of the interlayer charge density of pristine $H_{1-x}Ca_{2-x}La_xNb_3O_{10}$ is favourable for preparing the microporous semiconductive photocatalysts with the specific BET surface areas up to ~110 m^2/g . Ti K-edge XANES analysis reveals that the intercalation reaction occurs topotactically, followed by transformation into TiO_2 with rutile- and anatase-like local geometries depending upon the pillaring species.

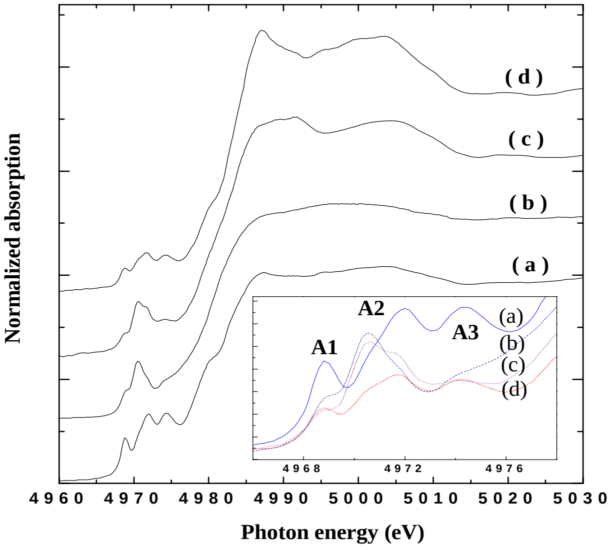

Figure 3
Fluorescence Ti K-edge XANES of the TiO_2 pillared calcium niobate using titanatrane complex; (a) anatase (reference), (b) titanatrane glycolate complex, (c) titanatrane intercalated $Ca_2Nb_3O_{10}$, and (d) heat-treated the sample (c) at 550°C for 3h.

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