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Composition-Dependent Ion-Exchange Reactivity of Potassium Lithium Titanates

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The ion exchange of dodecylammonium ion was examined for two potassium lithium titanates; the titanates were $K_{0.80}Ti_{1.71}Li_{0.29}O_{3.97}$ prepared by a solid-state reaction at 800 °C and $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$ prepared by a solid-state reaction at 1020 °C followed by reaction with aqueous H_2SO_4 and subsequent annealing. A single phase intercalation compound formed successfully for $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$ (the amount of the adsorbed dodecylammonium was 2.1 mmol g^{-1}) by reaction with an aqueous solution of dodecylammonium chloride. On the other hand, the parent titanate remained for $K_{0.80}Ti_{1.71}Li_{0.29}O_{3.97}$ (1.4 mmol g^{-1}).

Increasing attention has been paid to layered transition-metal oxides due to their cation exchange,[1] semiconducting,[2] and swelling properties.[3] Lepidocrocite-type titanates, whose general formula is represented as $A_xTi_{2-y}M_yO_4$ (A, interlayer cation; M, metal ion or vacancy), are characterized by versatility in composition.[4] Motivated by the successful swelling of titanate in aqueous solutions containing tetrabutylammonium ion,[5] reactions of titanates with inorganic and organic cations have actively been investigated recently.[6–16] The functionalization of layered titanates by the intercalation of guest species is a promising method, while quantitative ion exchange is still difficult after successful application of layer-by-layer deposition[17] or swelling-flocculation reaction[6e] to the titanates.

We report herein the composition-dependent controlled reactivity of potassium lithium titanates (KTLOs) toward an alkylammonium ion. The present finding will open up an opportunity to design properties of lepidocrocite-type titanates. The properties of layered clays such as ion-exchange and swelling clays depending on the layer charge density have been well documented.[18]

Experimental

Materials. Titanium dioxide (rutile) and alkali metal carbonates were of 99.9% purity or better, were purchased from Rare Metallic, Co., and used as received. Potassium chloride (≧99.5%) was purchased from Wako Pure Chemical Industries, Ltd. and used as received. Dodecylamine hydrochloride (>97%) was purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

Preparation of KTLOs. The preparation of KTLOs by solid-state reaction was conducted according to the literature;[6c] K_2CO_3, Li_2CO_3, and TiO_2 were ground in a molar ratio of $3x$:x:$(12-2x)$, where x denotes 0.85, 0.80, or 0.70, respectively, and the mixture was heated at 800 °C for 30 min in air to be decarbonated. After cooling, the mixture was ground and then heated at 800 °C for 20 h in air. Another reported procedure used in this study for the synthesis of KTLO involves the post-synthetic treatment of a KTLO synthesized by a solid-state reaction.[16] K_2CO_3, Li_2CO_3, TiO_2, and KCl were ground in a molar ratio of 2.2:0.73:9.5:1.8 and the mixture was heated at 1020 °C for 4 h in air. After cooling, the obtained powder (10 g) was dispersed in deionized water (200 mL) and to the slurry, 10 wt % aqueous H_2SO_4 solution was added dropwise at room temperature until the pH of the mixture plateaued at 7.0. The solid was separated by centrifugation (4000 rpm, 20 min), washed with deionized water, and dried under reduced pressure. The product thus obtained was heated at 600 °C for 3 h in air.

For controlling the composition of KTLO, the post-synthetic treatment using tuned amounts of aqueous H_2SO_4 was applied to a KTLO obtained by the above solid-state reaction at 800 °C ($x = 0.80$); to a slurry of KTLO (2.0 g) in water (200 mL), 1 wt % aqueous H_2SO_4 solution (1.5–32.3 mL) was added dropwise at room temperature until the pH of the mixture plateaued (11.0–6.0). The solid was separated by centrifugation (4000 rpm, 20 min), washed with deionized water, and dried under reduced pressure. The product thus obtained was heated at 600 °C for 3 h in air.

Reaction with Alkylammonium. Samples (0.20 g) were dispersed in an aqueous solution (50 mL) of dodecylamine (abbreviated as $C_{12}N^+$) hydrochloride (a molar $N/Ti_{2-y}Li_yO_4$ ratio of 1.0) and the mixture was stirred at room temperature for 2–3 h until the pH of the mixture plateaued. The reaction was conducted 1–3 times. The product was separated by centrifugation (4000 rpm, 20 min) then washed with deionized water.

Characterization. X-ray diffraction patterns of products were recorded on a Rigaku RAD IB powder diffractometer equipped with monochromatic Cu Kα radiation operated at 20 mA and 40 kV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on a Rigaku SPECTRO CIROS CCD. The products (10 mg) were decomposed for ICP measurement with 12 M H_2SO_4 (3.0 mL) at 150–200 °C for 2 h. Thermogravimetric and differential thermal analysis curves were recorded on a Rigaku TG8120 at a heating rate of 10 °C min^{-1} under air using α-Al_2O_3 as the standard material. The amount of the adsorbed dodecylammonium was calculated from the thermogravimetric curves of the products, where the mass loss due to oxidative decomposition from 150–800 °C was defined as the amount of inter-

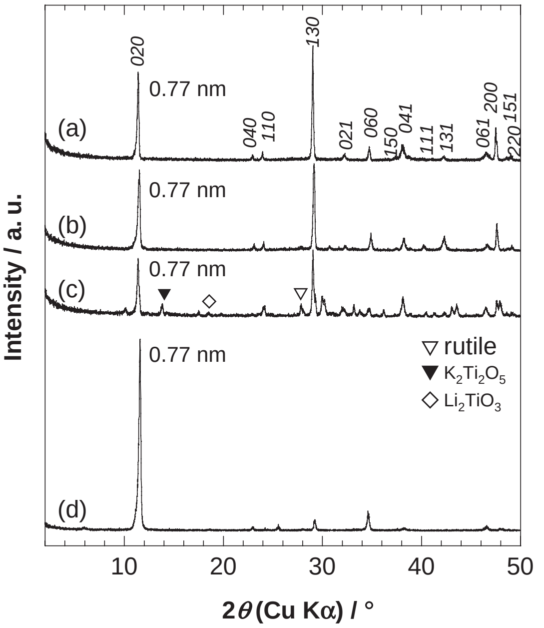

Figure 1. XRD patterns of KTLOs obtained by a solid-state reaction at 800 °C with different compositions of raw materials, $x =$ (a) 0.85, (b) 0.80, and (c) 0.70 in $K_xTi_{2-x/3}Li_{x/3}O_4$ and that obtained through treatment with a given amount of aqueous H_2SO_4 followed by heating of a KTLO prepared by a solid-state reaction at 1020 °C.

calated ammonium. Scanning electron micrograph (SEM) was obtained on a Hitachi S-2380N.

Results and Discussion

Comparison in Reactivity between Two KTLOs Synthesized by Reported Methods. Figures 1a and 1d depict the XRD patterns of KTLOs prepared by the reported methods, where all the observed diffraction peaks were ascribable to those of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$,[6c] indicating the formation of KTLOs. The compositions ($K_{0.80}Ti_{1.71}Li_{0.29}O_{3.97}$ and $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$) of the products were comparable to those ($K_{0.8}Ti_{1.73}Li_{0.27}O_4$ and $K_{0.7}Ti_{1.73}Li_{0.27}O_{3.95}$) reported in the literature.[6c,16]

Figure 2 shows the XRD patterns of $K_{0.80}Ti_{1.71}Li_{0.29}O_{3.97}$ and $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$ before and after the reaction with $C_{12}N^+$. For the $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$ system, a single phase product with basal spacing of 2.7 nm, which was increased from that of $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$ (0.77 nm), formed. A similar value of basal spacing has been reported for a dodecylammonium-exchanged $Rb_{0.75}Ti_{1.25}Mn_{0.75}O_4$ (2.7 nm)[9] and predicted from the basal spacings of the alkylammonium-exchanged $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (2.9 nm),[6c] indicating successful intercalation of $C_{12}N^+$ into $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$. While for the $K_{0.80}Ti_{1.71}Li_{0.29}O_{3.97}$ system, the parent titanate (or the protonated form) remained even after being reacted 3 times (Figure 2 inset).

Among possible factors for the different reactivity, such as variation in particle size (Figures 3a and 3b), we anticipated that variation in the composition, or the potassium content, played an important role. Accordingly, control of the composition of KTLOs was carried out for systematically investigating the composition–reactivity relationship of KTLOs. The heterogeneous composition of $K_{0.80}Ti_{1.71}Li_{0.29}O_{3.97}$ is another factor to be considered for different reactivity.

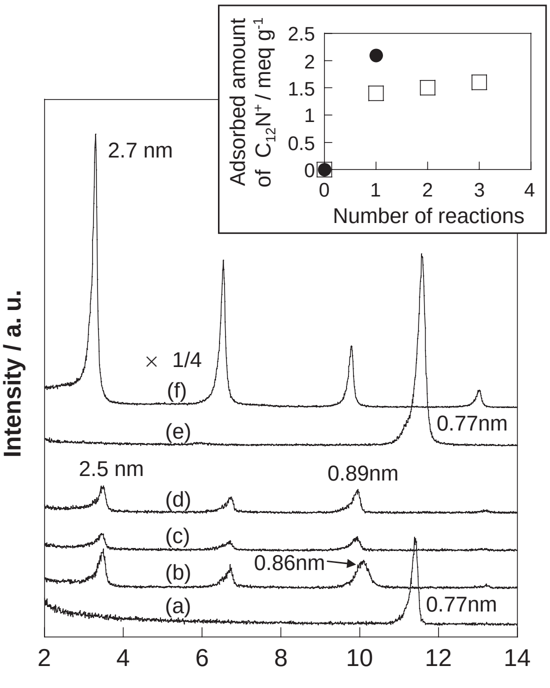

Figure 2. XRD patterns of $K_{0.80}Ti_{1.71}Li_{0.29}O_{3.97}$ (a) before and after the reaction with $C_{12}N^+$ for (b) 1, (c) 2, and (d) 3 times and $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$ (e) before and (f) after the reaction with $C_{12}N^+$ for 1 time. Inset: the variation of the adsorbed amount of $C_{12}N^+$ as a function of the number of reactions.

Control of Composition of KTLO. The control of the composition of KTLOs was first attempted by solid-state reaction at 800 °C with tuned composition of raw materials. Figures 1b and 1c show the XRD patterns of products obtained by decreasing x in $K_xTi_{2-x/3}Li_{x/3}O_4$, the amount of potassium in raw materials, from 0.85 to 0.80 and 0.70, respectively. A single phase KTLO with the composition $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ was obtained at $x = 0.80$ (Figure 1b). While at $x = 0.70$, rutile was isolated from the lepidocrocite phase. A similar result from the phase separation has been reported by Sasaki and co-workers, where single phase was obtained only at $x = 0.80$ among $x = 0.6$–1.0 in $K_xTi_{2-x/3}Li_{x/3}O_4$.[6c] By solid-state reaction, the control of the potassium content of KTLO was found to be difficult. Therefore, the post-synthetic procedure using tuned amounts of aqueous H_2SO_4 solution and subsequent heating was applied to $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ for controlling the composition. The successful formation of $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$[16] suggested to us that the potassium content in KTLO decreased and was controllable by changing the added amount of acid. The effect of heating after acidic treatment on the composition of KTLO, which has not been described in the literature,[16] was also investigated in this study.

The XRD patterns of the products obtained by the reaction between $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ and different amounts of aqueous H_2SO_4 solution are shown in Figure 4 together with that

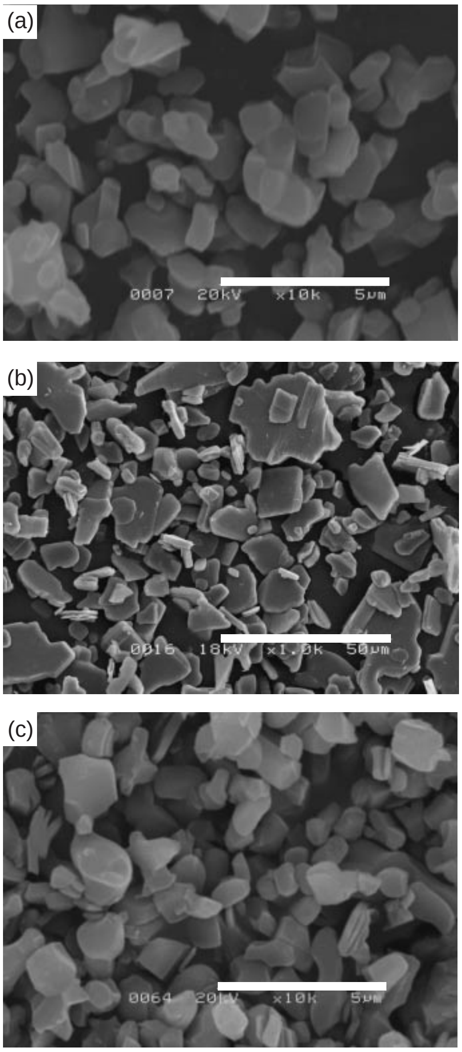

Figure 3. SEM images of (a) KTLO prepared by a solid-state reaction at 800 °C with the composition of raw materials, x in $K_xTi_{2-x/3}Li_{x/3}O_4 = 0.85$, and those prepared through H_2SO_4 treatment and subsequent heating at 600 °C of a KTLO synthesized by a solid-state reaction at (b) 1020 and (c) 800 °C with the composition of raw materials, x in $K_xTi_{2-x/3}Li_{x/3}O_4 = 0.80$. Scale bars: 5 μm for (a) and (c); 50 μm for (b).

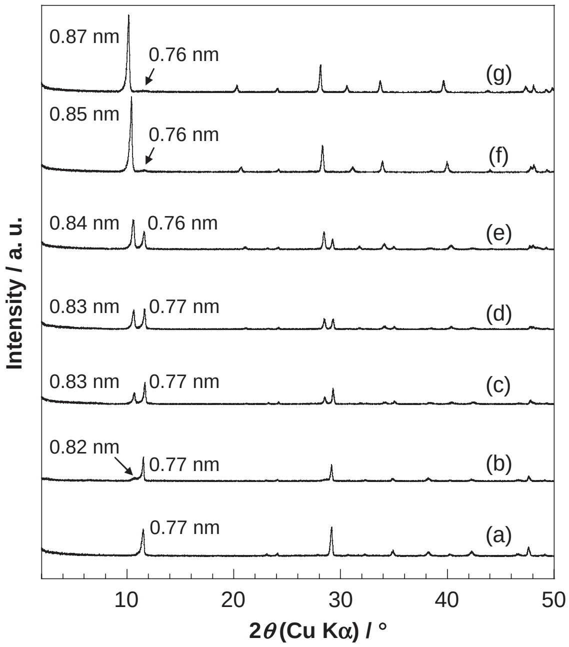

Figure 4. XRD patterns of (a) $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ and those treated with (b) 1.5, (c) 3.5, (d) 7.5, (e) 11.6, (f) 27.1, and (g) 32.2 mL of aqueous H_2SO_4 solution.

Table 1. Compositions of a KTLO Prepared by Solid-State Reaction at 800 °C and that Treated with Different Amounts of Aqueous H_2SO_4, and Those Subsequently Heated at 600 °C

Added amount of H_2SO_4/mL	Heating	Phase separation	Composition
—	—	—	$K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$
32.2	—	○	$K_{0.37}Ti_{1.79}Li_{0.21}O_{3.86}$
27.1	—	○	$K_{0.39}Ti_{1.76}Li_{0.24}O_{3.83}$
11.6	—	○	$K_{0.56}Ti_{1.72}Li_{0.28}O_{3.86}$
7.5	—	○	$K_{0.60}Ti_{1.72}Li_{0.28}O_{3.89}$
3.5	—	○	$K_{0.68}Ti_{1.72}Li_{0.28}O_{3.94}$
1.5	—	○	$K_{0.72}Ti_{1.73}Li_{0.27}O_{3.95}$
32.2	○	○	$K_{0.36}Ti_{1.79}Li_{0.21}O_{3.87}$
27.1	○	○	$K_{0.41}Ti_{1.77}Li_{0.23}O_{3.85}$
11.6	○	○	$K_{0.56}Ti_{1.72}Li_{0.28}O_{3.87}$
7.5	○	—	$K_{0.64}Ti_{1.72}Li_{0.28}O_{3.90}$
3.5	○	—	$K_{0.67}Ti_{1.72}Li_{0.28}O_{3.92}$
1.5	○	—	$K_{0.73}Ti_{1.72}Li_{0.28}O_{3.95}$

of the parent titanate, where the lepidocrocite structure of the titanate was retained upon reaction. As seen in Table 1, the potassium content in $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ decreased with the increase of added H_2SO_4. These results reveal that the interlayer potassium ion is extracted and the extracted amount is controlled by changing the added amount of H_2SO_4. A portion of potassium ion was exchanged with proton and/or oxonium ion, which was supported by the XRD patterns and TG-DTA curves of the products, wherein new diffraction peaks due to basal spacing larger than that of the parent titanate[6c] appeared upon reaction (Figure 4) and weight loss with endothermic peaks, which were ascribable to dehydration, were observed from 60 to 200 °C (Figure 5). It is thought that the composition of KTLO synthesized by solid-state reaction at 800 °C is heterogeneous and the more reactive phase (particles and/or interlayers) in the titanate is protonated upon reaction with H_2SO_4 aqueous solution leading to phase separation (Figure 4). Lithium ion in the host framework of potassium lithium titanates has been reported to completely be extracted by leaching the titanates in 1 M HCl ($M = mol\,dm^{-3}$) aqueous solution.[6c] In the present study, dilute acidic solution (pH $\geqq 6$) was used, therefore, the extraction of lithium ion from the titanate was suppressed (Table 1).

After heating, the composition of the H_2SO_4-treated products hardly changed (Table 1). Figure 6 depicts the XRD patterns of the heated products. At smaller amounts of added H_2SO_4, the corresponding heated products were single phase, whereas anatase and/or rutile were isolated from lepidocrocite phase at larger amounts of added acid. The products treated

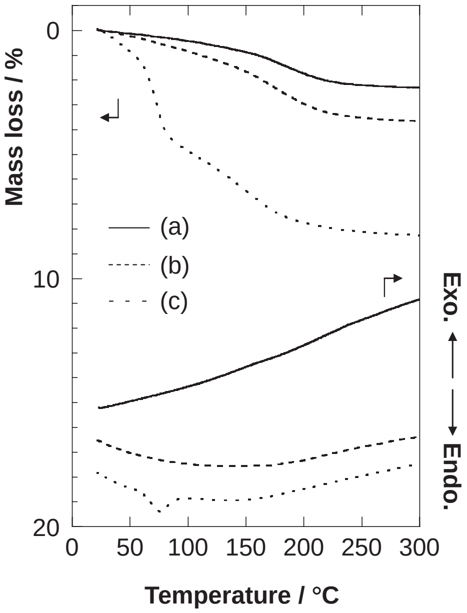

Figure 5. TG-DTA curves of $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ treated with (a) 7.5, (b) 11.6, and (c) 32.2 mL of aqueous H_2SO_4 solution. If all weight loss up to 200 °C is due to the desorption of interlayer water, the composition of the as H_2SO_4-treated titanates can be expressed as (a) $K_{0.60}Ti_{1.72}Li_{0.28}O_{3.89}\cdot 0.21H_2O$, (b) $K_{0.56}Ti_{1.72}Li_{0.28}O_{3.86}\cdot 0.34H_2O$, and (c) $K_{0.37}Ti_{1.79}Li_{0.21}O_{3.86}\cdot 0.82H_2O$, respectively.

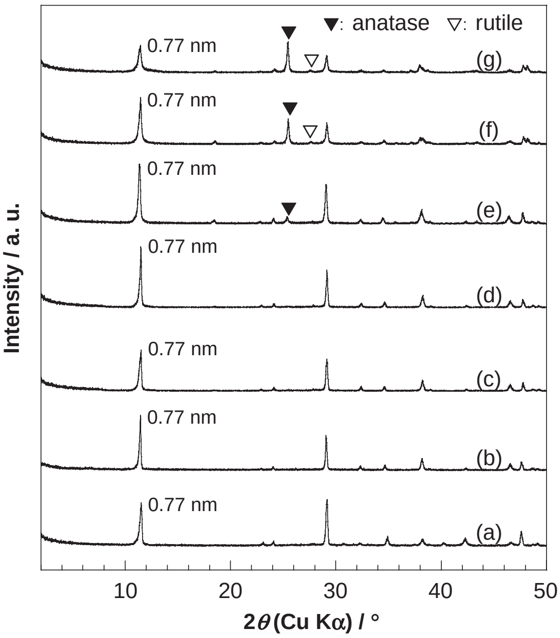

Figure 6. XRD patterns of (a) $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ and those treated with (b) 1.5, (c) 3.5, (d) 7.5, (e) 11.6, (f) 27.1, and (g) 32.2 mL of aqueous H_2SO_4 solution followed by heating at 600 °C.

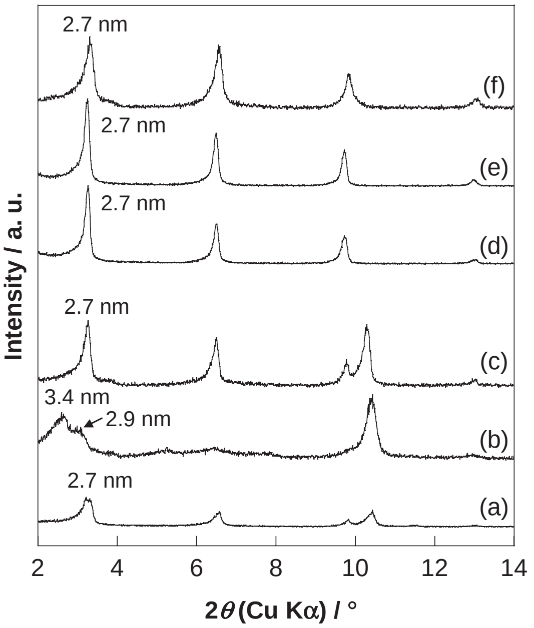

Figure 7. XRD patterns of KTLOs reacted with $C_{12}N^+$; (a)–(c) and (d) and (f) are $K_{0.78}Ti_{1.81}Li_{0.19}O_4$ treated with 1.5, 3.5, and 7.5 mL of aqueous H_2SO_4 solution and those subsequently heated, respectively.

with larger amounts of H_2SO_4 contained protonated titanate particles, and thus, the protonated titanates were transformed to anatase and rutile upon heating at 600 °C to lead to phase separation (Figures 6e–6g). While, for the products treated with smaller amounts of H_2SO_4, protonation occurred only within a particle, so that the isolation of bulk titania was suppressed.

Figure 3c depicts an SEM image of $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ treated with H_2SO_4 and subsequently heated. The platy morphology with a diameter of 1–2 µm of the parent titanate did not change upon reaction.

Reaction between KTLOs with Controlled Compositions and $C_{12}N^+$. Both the H_2SO_4-treated titanates and the corresponding heated titanates were reacted with $C_{12}N^+$. Figure 7 shows the XRD patterns of the products, wherein the basal spacing of the titanates increased to 2.6–2.9 nm from 0.77 nm upon reaction, indicating successful intercalation of $C_{12}N^+$ into the titanates.

Figure 8 indicates that the amount of adsorbed ammonium increases with the decrease in potassium content for the heated system, while that is irrelevant to the potassium content for the H_2SO_4-treated system. For heated titanates, it is thought that interlayer protons are removed, so that the amount of adsorbed ammonium reflects the composition (which correlates to the layer charge density). Lower potassium content and lower layer charge density make the electrostatic interaction between the titanate sheets weaker, leading to efficient intercalation of ammonium. Upon heating, the composition of the H_2SO_4-treated titanates was homogenized, which was supported by the single XRD pattern of the heated titanates reacted with ammonium (Figures 7d–7f). For the H_2SO_4-treated system, the protonated titanate particles were isolated as described above. Taking that a dominant driving force of the present cation exchange is an acid–base interaction between the interlayer alkali cation and the acidic solution of the ammonium ion into consideration, protons were prevented from being exchanged with

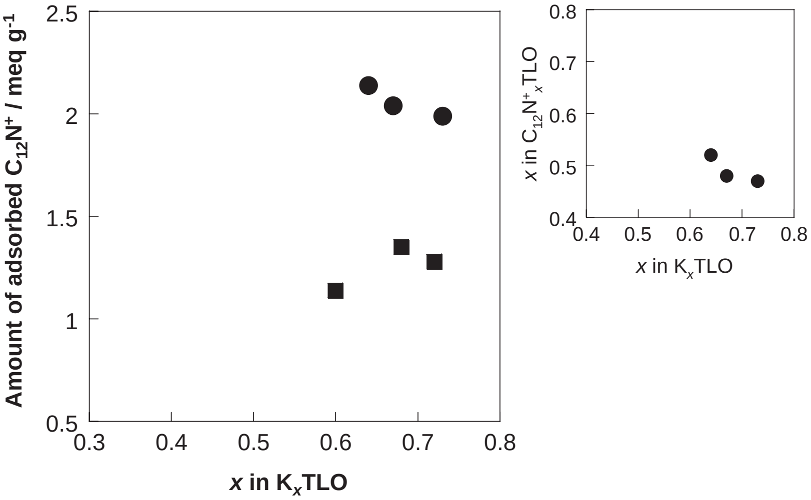

Figure 8. Variation in the adsorbed amount of $C_{12}N^+$ as a function of the potassium content of (■) H_2SO_4-treated titanates and (●) the corresponding heated titanates. Inset: Variation in the adsorbed amount of $C_{12}N^+$ as a function of potassium content in heated titanates.

the ammonium in acidic media. The potassium phase selectively reacted with the ammonium to result in the phase separation (Figures 7a–7c). Judging from the intensity of the diffraction peaks due to the protonated phase and the ammonium-exchanged phase for H_2SO_4-treated titanates, the titanates are thought to be composed of similar amounts of protonated and parent (potassium) phase. Therefore, the variation in the adsorbed amount of $C_{12}N^+$ between the H_2SO_4-treated titanates and the heated titanates by about two times is plausible (Figure 8).

The reaction of the heated titanates with dodecylammonium was not quantitative, which is shown in Figure 8 inset. A possible reason for the result is higher layer charge density of the heated titanates (0.31–0.36 $nm^2\,e^{-1}$) if compared with those of other layered solids whose reaction with organic molecular species has been reported to be quantitative[18] (e.g. smectites, 0.5–1 $nm^2\,e^{-1}$). The present post-synthetic treatment using $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ as the parent titanate is difficult for synthesizing titanates with potassium content lower than 0.64 per unit cell (equivalent to 0.36 $nm^2\,e^{-1}$) (Figure 9). However, $Rb_{0.75}Ti_{1.75}Li_{0.25}O_4$ and $Cs_{0.70}Ti_{1.77}Li_{0.27}O_4$ have been reported to be formed by solid-state reaction,[6c] and applying the present treatment to the two titanates, titanates with layer charge density lower than that of $K_{0.64}Ti_{1.72}Li_{0.28}O_{3.90}$ will be obtained to investigate the intercalation chemistry of lepidocrocite-type titanates.

Conclusion

We have reported the composition-dependent controlled reactivity of potassium lithium titanates toward an alkylammonium ion. The composition of the titanates has successfully been controlled through the reaction of a potassium lithium titanate obtained by a solid-state reaction with tuned amounts of aqueous H_2SO_4 solution followed by annealing.

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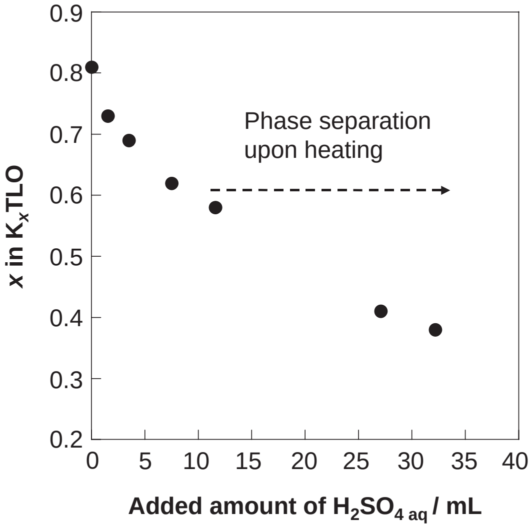

Figure 9. Variation in the potassium content of $K_{0.78}Ti_{1.81}Li_{0.19}O_{3.86}$ as a function of the added amount of aqueous H_2SO_4 solution.

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