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Molecular Recognitive Photocatalysis Driven by the Selective Adsorption on Layered Titanates

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Abstract: The composition of layered alkali titanates ($M_xTi_{2-x/3}Li_{x/3}O_4$; M = K^+, Li^+, Na^+) was tuned to control the swelling of the titanates in water and subsequently achieve molecular-sieve-like molecular recognitive photocatalytic decomposition of aqueous organic compounds on the titanates. Layered potassium lithium titanates with different layer charge density, $K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$, 0.67, and 0.74), was first synthesized and then the interlayer K^+ was quantitatively exchanged with Li^+ and Na^+ to form $Li_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$, 0.67, and 0.76) and $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$, 0.67, and 0.76). The water adsorption/desorption isotherms and X-ray diffraction patterns of the titanates revealed that the pristine K^+-type titanates hardly hydrated, while the Li^+- and Na^+-exchanged titanates expanded the interlayer space upon the hydration and the degree in the hydration was larger for the Na forms than for the Li ones and depended on the layer charge density. The present titanates were found to selectively adsorb benzene from an aqueous mixture of benzene, phenol, and 4-butylphenol and subsequently decompose benzene upon UV irradiation. The efficiency of the molecular recognitive photocatalytic benzene decomposition was related to the degree in the swelling of the titanates in water.

Introduction

Molecular recognitive reaction (or enzymatic reaction) in the photocatalysis of titanium dioxide is an intriguing topic for applications such as water purification and organic synthesis.[1,2] Efforts have been made to achieve selective photocatalytic reactions, while there are few successful reports. The control of substrates' access to active sites, or adsorption selectivity, is a potentially versatile methodology to impart substrate selectivity in the photocatalytic reaction on titanium dioxide. The mixing of titanium dioxide with β-cyclodextrin,[3] the coating of titanium dioxide particle with a molecular-imprinted organic polymer[4] or nanoporous silica,[5] and the immobilizing titanium dioxide finite particle in surfactant-templated mesoporous silica[6] have been conducted to create molecular recognition site on titanium dioxide. Besides the surface modification of titanium dioxide particle, the use of crystalline frameworks composed of titanium dioxide such as nanoporous titania-based compounds is a possible solution to selectively adsorb reactants. Accordingly, size (and partially polarity) selective photocatalytic decomposition[7] and organic transformation[8] over microporous titanosilicates have been reported. UV-light-induced organic synthesis on mesoporous titania with controlled pore diameter has also been conducted.[9] Due to the limited successes, the development of photocatalysts to preferentially recognize target molecular species is still worth investigating.

In this paper, we report an adsorption-driven molecular recognitive photocatalytic reaction over layered titanates. Layered titanates are unique materials for molecular recognitive reactions due to the expandable (swellable) two-dimensional interlayer space to accommodate a wide variety of molecular species. Efforts have been conducted to modify the reaction, such as visible light response by the complexation with photosensitizing complex ions[10] and improved efficiency by the lattice expansion (pillaring);[11] however, to the best of our knowledge, no report has been published about substrate selectivity, which is one of the important targets. Recently, we have reported molecular specific adsorption on the layered titanates modified with organic functional units, where the attached organic functional units may decompose upon UV light irradiaiton.[12] In this study, we conducted the photocatalytic reaction of benzene in an aqueous mixture of phenols using layered titanates to find a molecular-sieve-like photocatalytic decomposition of benzene over the titanates when the swelling in water was limited.

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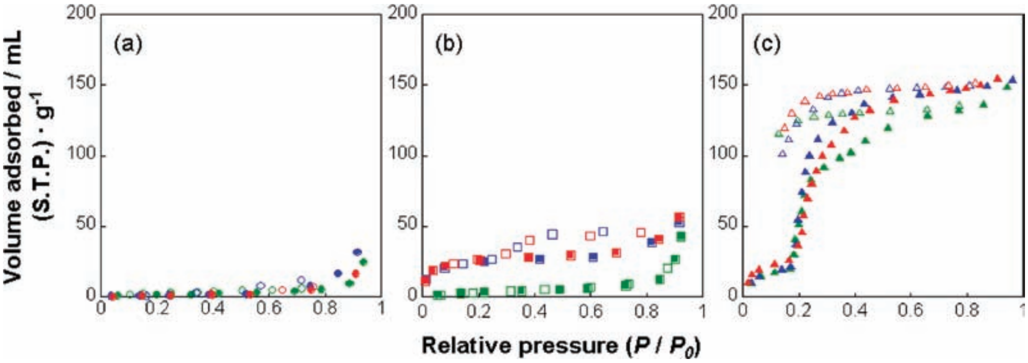

Figure 1. Water adsorption (filled symbol)/desorption (open symbol) isotherms of (a) $K_xTi_{2-x/3}Li_{x/3}O_4$ [$x =$ (red filled/open circle) 0.61, (blue filled/open circle) 0.67, (green filled/open circle) 0.74], (b) $Li_xTi_{2-x/3}Li_{x/3}O_4$ [$x =$ (red filled/open square) 0.61 (blue filled/open square) 0.67, (green filled/open square) 0.76], and (c) $Na_xTi_{2-x/3}Li_{x/3}O_4$ [$x =$ (red filled/open triangle) 0.61, (blue filled/open triangle) 0.67, (green filled/open triangle) 0.76].

Experimental Section

Materials. Titanium dioxide (rutile) and alkali metal carbonates, of 99.9% purity or better, were purchased from Rare Metallic, Co.. Lithium chloride (>99.95%), lithium hydroxide monohydrate (>95.0%), sodium chloride (>99.5%), sodium hydroxide (>95.0%), sulfonic acid (>96.0%), propylamine (>97.0%), benzene (>99.8%), and phenol (>99.0%) were obtained from Kanto Chemical Co., Inc. 4-Butylpnenol (>96.0%) was purchased from Tokyo Chemical Industry Co., Ltd. TiO_2 particles, AEROXIDE TiO_2 P25 (Nippon Aerosil), were used as a reference catalyst. All the chemicals were used as received.

Preparation of Layered Titanates. The preparation of layered potassium lithium titanates with different composition was conducted by a method similar to that developed in our earlier work.[13] A layered potassium lithium titanate was first synthesized by a solid-state reaction among K_2CO_3, Li_2CO_3, and TiO_2 with a molar ratio of 2.4:0.8:10.4. To the slurry of the titanate thus obtained (2.0 g) in water (200 mL), 1 mass % of the tuned amounts of aqueous solution of H_2SO_4 was added dropwise at room temperature until the pH of the mixture plateaued. The solid was separated by centrifugation (4000 rpm, 20 min), washed with water, and dried under reduced pressure. The product thus obtained was heated at 600 °C for 3 h in air to form $K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$, 0.67, and 0.74).

The incorporation of Li^+ or Na^+ into $K_xTi_{2-x/3}Li_{x/3}O_4$ was conducted by the reaction of the titanates (or the corresponding protonated forms) with an aqueous solution (200 mL) containing the alkali ions (a molar ratio of Li/K or Na/K = 2.0). The mixture was stirred under room temperature until the pH of the mixture plateaued. The reaction was conducted one to three times. The product was separated by centrifugation (4000 rpm, 20 min) and washed with water. For the preparation of the Na^+-exchanged titanate, ion exchange reaction in the presence of propylamine (a molar N/K ratio = 2.0) was also conducted.

Photocatalytic and Adsorption Tests. A 4.0 mg portion of the catalyst was added to 40 mL of a mixed aqueous solution of benzene, phenol, and 4-butylphenol (6.0 ppm) in a quartz vessel. The adsorption of the substrates onto the catalyst reached equilibrium, and subsequently, the mixture was irradiated with an ultra-high-pressure mercury lamp (350 W, Ushio Inc.) under magnetic stirring. The supernatant was separated by centrifugation (25 000 rpm, 10 min), and the amount of the residual substrates was determined from the remaining amount in the supernatant. Photocatalytic conversion of aqueous benzene to phenol was conducted in a similar way, except that 4.0 mg of the catalyst and 40 mL of aqueous benzene solution (6.0 ppm) were used. Adsorption isotherms were prepared as follows: The catalyst (4.0 mg) was added to 0.38−6.0 ppm of an aqueous mixture of benzene, phenol, and 4-butylphenol (40 mL) and the mixture was shaken for 12 h at room temperature. After the mixture was separated by centrifugation (25 000 rpm, 10 min), the amount of the adsorbed substrates on the catalyst was determined on the basis of the remaining amount in the supernatant.

Characterizations. 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. Prior to the measurements, the K- and Na-type titanates and Li-type titanate were heated at 200 and 120 °C, respectively. When measuring with the hydrated titanates, powder sample (7.0 mg) was put in a glass holder and filled with water (50 μL) to obtain a slurry and the slurry was covered with poly(ethylene terephthalate) film to prevent solvent evaporation during the measurement. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on a Rigaku SPECTRO CIROS CCD. The products (10 mg) were decomposed for the ICP measurement with H_2SO_4 (3.0 mL) at 150−200 °C for 2 h. Water vapor adsorption/desorption measurements were carried out at 25 °C using a BELSORP MAX apparatus. Prior to the measurement, sample was outgassed at 120 °C for 3 h under vacuum. High-performance liquid chromatography was performed on Shimadzu SCL-10Avp equipped with a UV detector.

Results and Discussion

In order to control the swelling of layered titanates, we tuned the composition of layered titanates, which was motivated by the fact that the hydration and swelling of smectite group of layered clay minerals depended on the composition (interlayer cation and layer charge density).[14,15] In this study, layered titanates, $K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$, 0.67, and 0.74, these values directly correlate to the layer charge density), were used as the starting materials.[13] The pristine titanates were allowed to react with aqueous solutions containing Li^+ or Na^+ to exchange the interlayer K^+ with the alkaline metal ions. The interlayer K^+ of $K_xTi_{2-x/3}Li_{x/3}O_4$ was quantitatively replaced with Li^+ ($Li_xTi_{2-x/3}Li_{x/3}O_4$; $x = 0.61$, 0.67, and 0.76) by the ion exchange reaction between the protonated titanate and an aqueous LiOH solution. On the other hand, Na^+ was exchanged quantitatively ($Na_xTi_{2-x/3}Li_{x/3}O_4$; $x = 0.61$, 0.67, and 0.76) only when $K_xTi_{2-x/3}Li_{x/3}O_4$ was allowed to react with an aqueous NaOH solution containing propylamine. The K^+-type titanates did not hydrate to increase the interlayer space (Figures 1a and 2a), accordingly, the pre-expansion of the interlayer space with the intercalation of propylamine was required for relatively large

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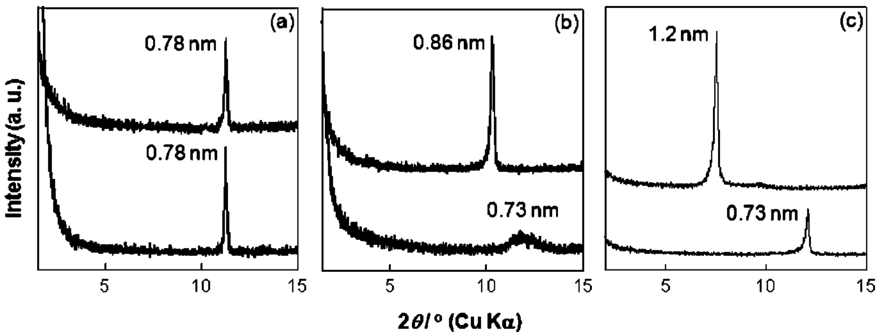

Figure 2. X-ray diffraction patterns of (a) $K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.67$), (b) $Li_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.67$), and (c) $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.67$) before (lower) and after (upper) the reaction with water.

and high-hydration energy Na^+ to effectively be incorporated in the titanate from water. From the basal spacing and composition of the Na^+-exchanged titanates, propylamine was completely removed from the interlayer space of the products. The guest-replacement method using alkylammonium ions has been often utilized for the intercalation of bulky ions like organic dyes into layered solids with poor swelling ability.[16]

Figure 1 shows the water vapor adsorption/desorption isotherms of $K_xTi_{2-x/3}Li_{x/3}O_4$ and the corresponding Li^+- and Na^+-exchanged titanates. The original K^+-type titanates hardly adsorbed water; however, the adsorption capacity of water was remarkably enhanced when the interlayer K^+ of the titanate was replaced with Li^+ or Na^+. The amounts of adsorbed water were larger on $Na_xTi_{2-x/3}Li_{x/3}O_4$ than on $Li_xTi_{2-x/3}Li_{x/3}O_4$ and were dependent on the amount (which directly correlates to the layer charge density) of the interlayer cation. The similar tendency was observed for the X-ray diffraction patterns of the hydrated titanates; $K_xTi_{2-x/3}Li_{x/3}O_4$ did not expand the interlayer space upon the reaction with water. On the other hand, the Li^+- and Na^+-exchanged titanates hydrated to increase the basal spacing, and the degree of the increase was larger for $Na_xTi_{2-x/3}Li_{x/3}O_4$ than for $Li_xTi_{2-x/3}Li_{x/3}O_4$ (Figure 2). Thus, the interlayer expansion of the layered titanates upon hydration was successfully controlled by tuning the composition. Similar phenomena for the composition-dependent hydration and swelling in water have been reported for smectite clays.[14,15] It has been reported that the replacement of the interlayer K^+ of a nonswelling layered clay, muscovite, with Li^+ let the clay hydrate to expand the interlayer space, which allows for the intercalation of a bulky organic cation.[17]

Norrish has proposed that the swelling in water of layered solids depends on the ratio of repulsive potential, which correlates to the hydration energy of the interlayer ions, to attractive potential, which is proportional to σ/D, where σ and D are the layer charge density and the distance between the neighboring oxide sheets, respectively, and experimentally confirmed that the degree of the swelling of a series of montmorillonite with varied interlayer cations is directly related to the hydration energy of the cations.[15] In the present system, the swelling of the present titanates did not depend on the hydration energy of the interlayer cations (Li^+, 136 kcal g^{-1} ion^{-1}; Na^+, 114 kcal g^{-1} ion^{-1}; K^+, 94 kcal g^{-1} ion^{-1}).[18] The K^+-type titanate did not hydrate to swell, which was explained by the low hydration energy of K^+. On the other hand, the reason for the effective hydration of the titanates exchanged with Na^+, whose hydration energy is between the three alkali metal ions, is not clear at present. Other factors such as the difference in size in the interlayer cation (Li^+, 0.12 nm; Na^+, 0.19 nm; K^+, 0.26 nm)[19] may affect the repulsive potential and attractive force of the neighboring titanate sheets.

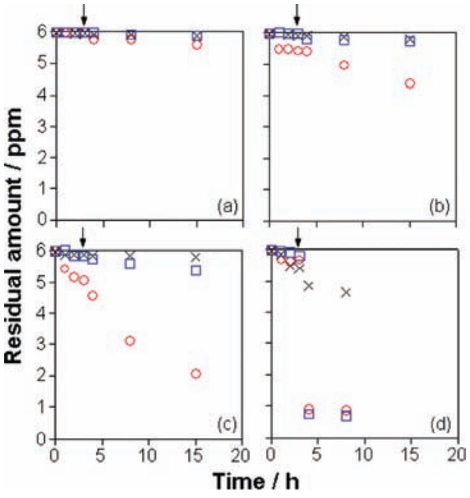

Figure 3. Photocatalytic decomposition of (red circles) benzene, (blue squares) phenol, and (black ×'s) 4-butylphenol in their aqueous mixture by (a) $K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.74$), (b) $Li_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.76$), (c) $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$), and (d) titanium dioxide (P25). Arrows indicate the beginning of ultraviolet light irradiation.

On the basis of the above results, we considered that the present titanates exhibited controlled and limited swelling in water to recognize a certain kind of molecule with the size close to the gallery height in water (swollen state). Therefore, the titanates with different composition, $K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.76$), $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.76$), and $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$), were used as photocatalysts for the decomposition of organic compounds with different molecular size, benzene ($0.6 \times 0.6 \times 0.3$ nm^3), phenol ($0.6 \times 0.7 \times 0.3$ nm^3), and 4-butylphenol ($0.6 \times 1.1 \times 0.4$ nm^3), in aqueous solution. As shown in Figure 3, the K^+-type titanate hardly adsorbed any substrates from the aqueous mixture, while the Na^+-exchanged titanates selectively adsorbed benzene from the aqueous mixture and decomposed

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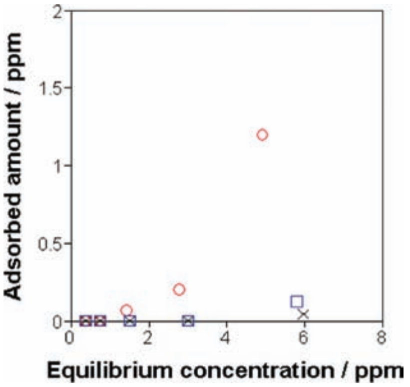

Figure 4. Adsorption isotherms of (red circles) benzene, (blue squares) phenol, and (black ×'s) 4-butylphenol from the aqueous mixture on $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$).

it upon UV irradiation. $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$) adsorbed and decomposed benzene more effectively than $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.76$) did. The distance of the adjacent titanate sheets in water for $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$) is largest among the three titanates, which is predicted by Figure 1; accordingly, benzene with a size ($0.6 \times 0.6 \times 0.3$ nm^3) smaller than the gallery height ($\geq$0.7 nm) of the titanate is thought to access to the interlayer surface to be photocatalytically decomposed.

The adsorption isotherms of the three substrates from the aqueous mixture on the Na^+-type titanate showed that the benzene isotherm exhibited S-type, while phenol and 4-butylphenol hardly adsorbed (Figure 4). On the basis of the interlayer surface area (ca. 760 m^2 g^{-1}, calculated on the basis of the chemical composition[14]) of the catalysts and the amount of the consumed reactants, the effect of the particle surface (surface area is not more than a few of tens m^2 g^{-1}) on the present photocatalysis is negligible; for example, the amount of the adsorbed benzene on $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$) before UV irradiation was ca. 0.13 groups per $Ti_{2-x/3}Li_{x/3}O_4$ (equivalent to ca. 20% per the interlayer Na^+). Moreover, as shown in Figure 5, phenol hardly formed when the Na^+-type titanate was reacted with aqueous benzene under UV light irradiation. These facts support that the present molecular selective photocatalysis is due to a size-exclusive effect. It is worth mentioning that the molecular recognitive photocatalytic benzene decomposition is not achieved on a commercially available titanium dioxide (Figure 3d).

The control of reactants' access to active sites is a possible solution to achieve molecular recognitive catalysis. The embedment of titanium dioxide particles (P25) with nanoporous silica with pore diameter of 2.7 nm has been reported to selectively decompose 4-nonylphenol in aqueous mixture containing 4-nonylphenol, 4-heptylphenol, and 4-propylphenol, which is explained by the hydrophobic surface of the silica.[6] The molecular-sieve-like photocatalytic oxidation of 1,2,4-trisubstituted chlorophenols by microporous titanosilicates, TS-1 (pore diameter of 0.52 nm × 0.58 nm) and TS-2 (0.53 nm × 0.54 nm),[8a] and the size- and polarity-driven selective photo-oxidation of benzene, toluene, and 2,5-dichlorophenol over another microporous titanosilicate, ETS-10 (pore diameter of 0.76 nm × 0.49 nm),[8b] have also been investigated. If compared with materials ever reported,[3−9] the present titanates could be a versatile photocatalyst to achieve molecular recognitive photocatalysis of a wide variety of molecular species in water, since the interlayer expansion of the titanate in water is controlled with not only the composition but also electrolyte concentration in water.[14,15,20] In addition, the idea is applicable to various layered materials,[21] and the present success opens up a new opportunity for molecular recognition and selective photocatalytic reactions.

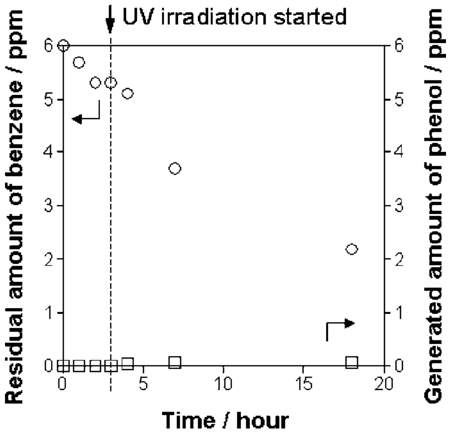

Figure 5. Photocatalytic conversion of aqueous benzene to phenol on $Na_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.61$).

Conclusions

We have found a unique and useful molecular recognition phenomenon in the photocatalytic decomposition of organic compounds using layered titanates. This was achieved by the careful examination using layered titanate with controlled composition ($M_xTi_{2-x/3}Li_{x/3}O_4$; $M = K^+, Li^+, Na^+$), which directly correlate with the swelling ability. The sodium form of layered titanates selectively adsorbed and decomposed benzene in water containing benzene, phenol, and 4-butylphenol, which reflected the degree in the interlayer expansion in water.

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