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Protonated Titanate Nanotubes as Solid Acid Catalyst

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Lewis acid catalysts such as $AlCl_3$ and BF_3 are essential in many industrially important reactions, such as the synthesis of ethylbenzene, linear alkyl benzene, cumene, and aromatic ketones. Although such homogeneous acid catalysts are highly active, they have serious drawbacks, such as the production of waste, separation from the product, and corrosion of equipment. From the viewpoint of the environmentally benign chemical process, the use of solid acid catalysts has been required to minimize the emission of toxic byproducts.[1] Metal oxides are utilized for both their acid−base and redox properties and constitute the largest family of catalysts in heterogeneous catalysis.[2] We have focused on titanium oxide as a solid acid catalyst, because titanium dioxide contains Lewis acid sites and titanium is the second most abundant transition metal (ninth of all elements) in the Earth's crust. Among titanium oxide materials, titanate nanotubes have attracted much attention due to their unique physicochemical properties and unusual morphology.[3] Titanate nanotubes are synthesized by the hydrothermal treatment of TiO_2 in a basic aqueous solution, followed by H^+-exchange, a simple method requiring neither expensive apparatus nor special chemicals. The scrolling of an exfoliated layered titanate nanosheet results in the nanotube structure during hydrothermal treatment. Titanate nanotubes have been extensively investigated in areas such as catalysis, photocatalysis, electrocatalysis, sensors, and lithium batteries.[3] In the field of catalysis, most of the studies for the material are directed toward the utilization of the material as a support with a large surface area.[3] However, the acid catalytic properties of the titanate nanotube itself have not yet been investigated in detail. In this study, protonated titanate nanotubes were studied as a solid acid catalyst for potential application to the environmentally benign production of chemicals. The material exhibits remarkable catalytic performance as a Lewis acid catalyst with active Brønsted acid sites.

Figure 1a shows a high resolution transmission electron microscopy (HRTEM) image of the resulting material. The tube structures of *ca.* 10 nm in outer diameter and *ca.* 5 nm in inner diameter are observed. The interlayer spacing of protonated titanate nanotubes is *ca.* 0.7 nm (Figure 1b), which is close to the value reported in the literature.[3,4] The nitrogen adsorption−desorption analysis revealed that protonated titanate nanotubes have a high density of mesopores with a narrow distribution (2−10 nm) (Figure S1). The mesopore sizes are approximately equal to the pore diameter observed by HRTEM. The specific surface area calculated from the isotherm was approximately 400 $m^2\ g^{-1}$, which is larger than that of the starting material (300 $m^2\ g^{-1}$).

The catalytic performance of the protonated titanate nanotubes was examined through the Friedel−Crafts (FC) alkylation of toluene with benzylchloride, a liquid phase test reaction. Figure S2 shows the time courses of benzyltoluene production over protonated titanate nanotubes at 373 K. For comparison, the results for the conventional solid acid catalysts are also shown. The formation of *o*-benzyltoluene and *p*-benzyltoluene was observed in all catalysts (Table S1). In the case of ion-exchange resins, the yields of benzyltoluene after 1 h do not even reach 5%. On the other hand, protonated titanate nanotubes, TiO_2, $Nb_2O_5 \cdot nH_2O$, SO_4^{2-}/ZrO_2, and zeolites all exhibited superior activity to that of ion-exchange resins. These inorganic solid acids possess Lewis acid sites[1] that play an important role in determining the catalytic activity for this reaction, because FC alkylation of aromatic rings and alkyl halides proceed effectively over a Lewis acid catalyst rather than a Brønsted acid catalyst.[5] Figure 2 shows the catalytic activity of each catalyst at near room temperature (300 K). At 300 K, almost all of the conventional catalysts displayed negligible catalytic activity, and even the catalytic activities of SO_4^{2-}/ZrO_2 and H*β* were moderate. In contrast to the conventional catalysts, the titanate nanotubes exhibit remarkable catalytic performance for the reaction at 300 K; the yield of benzyltoluene reached 90% at 180 min. Assuming that the reaction is catalyzed only on Lewis acid sites, the turnover number at 180 min

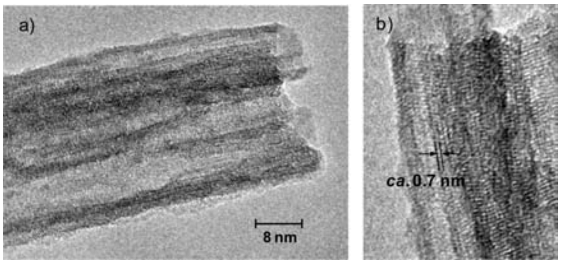

Figure 1. (a) HRTEM image of the protonated titanate nanotubes. (b) Enlarged HRTEM image of (a).

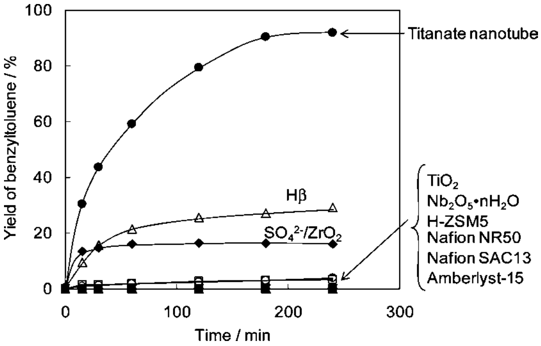

Figure 2. Time courses of benzyltoluene formation using various solid acid catalysts. Reaction conditions: catalyst (0.2 g), toluene (0.1 mol), benzylchloride (0.02 mol), reaction temperature 300 K.

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Table 1. Friedel−Crafts Alkylation over Various Nanostructured Titanate Materials[a]

Catalyst	Surface area [m^2 g^{-1}]	V_p [cm^3 g^{-1}][b]	Yield [%][c]
Titanate nanotube	400	0.74	92.0
Titanate nanosheet	106	0.31	7.6
Layered titanate	5	−	0.0

[a] Reaction conditions: catalyst (0.2 g), toluene (0.1 mol), benzylchloride (0.02 mol), reaction temperature 300 K. [b] Total pore volume. [c] Yield of benzyltoluene.

was estimated to be *ca.* 320 (see below). No byproducts were observed in the solution after the reaction using titanate nanotubes. The titanate nanotubes were recoverable by filtration and washing, and the recovered solid acid was confirmed to be reusable without a significant decrease in catalytic activity (Figure S3). Although HCl is formed during the FC reaction, it was confirmed that HCl and H_2SO_4 cannot catalyze the FC reaction at 300 K (Figure S4). $AlCl_3$ is a highly active homogeneous Lewis acid that has been used for the production of industrially important chemicals but is not reusable and has a much higher catalytic activity for the reaction than titanate nanotubes, with the conversion of benzylchloride reaching *ca.* 100% within 1 h at 300 K. However, the benzyltoluene yield cannot exceed 70%, due to the formation of byproducts from the further alkylation of reactants and products.

The difference FT-IR spectra of pyridine-adsorbed TiO_2 and protonated titanate nanotubes (298 K) are shown in Figure S5. The bands observed at *ca.* 1450 cm^{-1} in both spectra of TiO_2 and the titanate nanotubes are assignable to pyridine coordinatively bound to Lewis acid sites.[6] The band at *ca.*1540 cm^{-1}, due to pyridinium ions formed by Brønsted acid sites,[6] was not observed for TiO_2, but only for titanate nanotubes, which indicates that protonated titanate nanotubes possess both Brønsted and Lewis acid sites. The concentrations of Brønsted and Lewis acid sites on the titanate nanotubes were estimated to be 0.10 and 0.25 mmol g^{-1}, respectively (see the Supporting Information). The results suggest that the efficient reaction on protonated titanate nanotubes is due to not only the Lewis acid sites but also the active Brønsted acid sites. The reaction was further investigated using Na^+-exchanged titanate nanotubes prepared by the cation exchange of protonated titanate nanotubes in an aqueous NaOH solution. This material only with Lewis acid sites (Figure S6) showed high catalytic performance at 373 K as shown in Table S2. However, it cannot function at 300 K. Apparently, the alkylation by the Lewis acid sites at room temperature does not proceed without the Brønsted acid sites. Such synergy between Brønsted and Lewis acid sites has been reported to enhance the catalytic activity in isomerization, cracking, and FC alkylation.[7] In many cases, it is expected that the synergy facilitates carbocation formation by acidity enhancement, resulting in high catalytic activity.[7] The Brønsted acid sites may also promote carbocation formation with the formation of HCl at room temperature although the details are currently under investigation.

It should be noted that titanate nanosheets, such as $H_2Ti_3O_7$ which has a similar crystal structure of titanate nanotubes,[4] do not have high catalytic activity for the FC reaction, although protonated titanate nanotubes are formed from these titanate nanosheets.[3] The catalytic performance of layered $H_2Ti_3O_7$, $H_2Ti_3O_7$ nanosheets, and titanate nanotubes for the FC alkylation of toluene with benzylchloride at 300 K is summarized in Table 1. In the case of layered $H_2Ti_3O_7$, the reactants cannot approach the Ti−OH groups in narrow interlayer spaces, resulting in no catalytic activity. Although many Ti−OH groups can be exposed to the reactants in aggregated $H_2Ti_3O_7$ nanosheets prepared by the aggregation of exfoliated $H_2Ti_3O_7$ nanosheets from layered $H_2Ti_3O_7$,[8] this FC alkylation does not proceed efficiently on the nanosheet material. Figure S7 shows the results for the formation of 5-hydroxymethylfurfural (HMF) from glucose and fructose on solid acid catalysts, including protonated titanate nanotubes and $H_2Ti_3O_7$ nanosheets. HMF, a key molecule in biorefinery, can be converted into fine chemicals, pharmaceuticals, diesel fuel additives, and various bioderived polymers,[9] and HMF formation from glucose and fructose has been extensively studied using various Brønsted acid catalysts such as mineral acids, ion-exchange resins, and zeolites.[10] Protonated titanate nanotubes exhibited a much higher catalytic performance for the reactions than the tested conventional solid acids, including resins, zeolites, and $H_2Ti_3O_7$ nanosheets. Because both reactions proceed through the dehydration of fructose, Brønsted acids promote these reactions, indicating that titanate nanotubes have more effective Brønsted acid sites than the other solid acids. These results indicate that the amount of effective Brønsted acid sites on $H_2Ti_3O_7$ nanosheets is much smaller than that of titanate nanotubes, which suggests that scrolling of the exfoliated titanate nanosheets forms Brønsted acid sites available for the FC reaction and HMF formation. Silanol groups (Si−OH) are typically neutral functional groups in many SiO_2 materials. However, Si−OH groups in some SiO_2 materials with mesopores, such as FSM-16 and MCM-41, do function as relatively strong Brønsted acid sites,[11] which can be attributed to distortion of the lattice.[11] Therefore, lattice distortion due to the scrolling of titanate nanosheets may form effective Brønsted acid sites.

In summary, protonated titanate nanotubes function as a highly active heterogeneous Lewis acid catalyst, due to effective Brønsted acid sites on the scrolled titanate nanosheets, large amounts of Lewis acid sites, and large pores.

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Supporting Information Available: Experimental section, Table S1−S2, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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