

## Catalytic reactions of organic compounds by titanium oxides and titanate nanotubes

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Heterogeneous catalysts are necessary to establish environmentally friendly process because they are reusable and easy to separate from reaction mixture. In this thesis, the protonated titanate nanotube catalysts for Friedel-Crafts alkylation of aromatic compounds and the metal loaded TiO<sub>2</sub> photocatalysts for photocatalytic cyanomethylation and lactonization were studied.

In Chapter 1, acid-catalyzed organic reactions and photocatalytic organic reactions were shortly reviewed to remind the background of this thesis. In case of the acid catalyzed reactions, some examples of acid catalyzed reactions promoted by heterogeneous catalysts were mentioned. Among them, it was noted that some of reactions are cooperatively enhanced by two kinds of the acids sites, Brønsted acid sites and Lewis acid sites. It was also mentioned that catalytic performance is controlled by the structure of catalysts, *i.e.*, the pore size of the material or interlayer distance affects the catalytic ability. As for photocatalytic organic reactions, it was described that some studies have been reported successive photocatalytic organic synthesis by Pt/TiO<sub>2</sub> photocatalyst or Pd/TiO<sub>2</sub> bifunctional catalyst in the absence of oxygen. Finally, the outline of this thesis was introduced.

In Chapter 2, it was demonstrated that Brønsted acid sites of protonated titanate nanotubes is stronger than that of titanate nanosheets such as H<sub>0.7</sub>Ti<sub>1.825</sub>O<sub>4</sub>·H<sub>2</sub>O and H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. Titanate materials such as layered titanate, nanosheets, and nanotubes were applied for the Friedel-Crafts alkylation of toluene with benzyl chloride and the reaction was well promoted by protonated titanate nanotubes, however, both of nanosheets hardly enhanced the reaction. The results of MAS NMR and FT-IR analysis suggested that titanate nanotubes has Brønsted acid sites stronger than other materials, while Lewis acid strength of titanate nanotube

is almost the same as titania nanosheets, which originates from the tube structure with torsion. This hypothesis was supported by the results of DFT calculation using ammonia as a probe molecule. Since other titanate materials except for the titanate nanotubes did not promote the reaction at room temperature, the strong Brønsted acid sites on the nanotube should assist the reaction.

In Chapter 3, hydrothermally treated titanate materials were prepared at various temperatures and applied for Friedel-Crafts alkylation of toluene with benzyl alcohol or benzyl chloride. Anatase nanoparticles were converted into various titanate structures by the hydrothermal treatment, and the nanotube structure was formed at 423 K. The nanotube significantly enhanced the Lewis catalyzed reaction of toluene and benzyl chloride, but other titanate materials and anatase  $\text{TiO}_2$  nanoparticles showed poor catalytic activity for the reaction. The FT-IR analysis with a base molecule revealed that all titanate materials have Lewis acid sites, but only the nanotube has Brønsted acid sites. The result of Brønsted acid catalyzed reaction of toluene and benzyl alcohol supported the hypothesis that titanate nanotube has effective Brønsted acid sites. In addition, it was confirmed that  $\text{Na}^+$  exchanged titanate nanotube cannot promote both of the Lewis and Brønsted acid catalyzed reactions. Thus the cooperative work of Lewis acid sites and Brønsted acid sites on the titanate nanotube well enhances the Friedel-Crafts alkylation at room temperature.

In Chapter 4, Nb doped titanate nanotube (Nb-TiNT) samples were synthesized by hydrothermal treatment of Nb doped  $\text{TiO}_2$  prepared by a sol-gel method. XRD patterns and the results of  $\text{N}_2$  adsorption measurements of the Nb-TiNT samples suggested that the nanotube structure forms regardless of Nb amounts. However, the TEM/EDX images and the results from ICP-AES analysis revealed that Nb cations also formed amorphous Nb oxides particles on the surface of the Nb-TiNT samples. However, the Lewis acid catalyzed reaction between toluene and benzyl chloride was significantly enhanced over the Nb-TiNT samples compared to the

non-doped TiNT sample. Furthermore, the Brønsted acid catalyzed reaction of toluene with benzyl alcohol was also enhanced over the Nb-TiNT samples, which suggests the existence of doped Nb atoms in the titanate nanotubes framework. Since the catalytic activity of Nb-containing solid acid catalysts such as  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  and Nb-Ti mixed oxides, and the physical mixture of  $\text{Nb}_2\text{O}_5$  and TiNT was lower than that of the Nb-TiNT samples, Nb cations were partially doped into nanotubes to generate Brønsted acid sites such as  $\text{Ti}(\text{OH})\text{Nb}$ .  $^{31}\text{P}$  MAS NMR and FT-IR measurements with base probe molecules evaluated that acid amount of both of the Nb-TiNT samples and the TiNT sample was almost the same, but the strong Brønsted acid sites increased on the Nb-TiNT samples. Since the pore size distributions of the Nb(5%)-TiNT sample was narrower than that of the TiNT sample, it can be concluded that strong Brønsted acid sites and uniformed pore distributions were formed by adding Nb, resulting the high catalytic activity of the Nb-TiNT samples for Friedel-Crafts alkylation of aromatic compounds.

In Chapter 5, the direct cyanomethylation of hydrocarbons with acetonitrile over metal loaded  $\text{TiO}_2$  photocatalyst ( $\text{M}/\text{TiO}_2$ ) or physical mixture of  $\text{M}/\text{TiO}_2$  photocatalyst and metal loaded  $\text{Al}_2\text{O}_3$  ( $\text{M}/\text{Al}_2\text{O}_3$ ) was demonstrated. The  $\text{M}/\text{TiO}_2$  samples were prepared with photodeposition method, and the  $\text{M}/\text{Al}_2\text{O}_3$  samples were prepared with impregnation method. The  $\text{Pt}/\text{TiO}_2$  photocatalyst promoted the cyanomethylation of cyclohexane and cyclohexene more than the  $\text{Pd}/\text{TiO}_2$  photocatalyst. In addition, a physical mixture of the  $\text{Pt}/\text{TiO}_2$  photocatalyst and the  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst was not improved the yield of cyanomethylated compounds. Thus the catalytic property of the Pd metal particles, which was observed in the cyanomethylation of benzene, did not contribute to produce cyanomethylated cyclohexane and cyclohexene. In these reactions, the oxidation of reactants by holes competitively occur to form the corresponding radical species, followed by the radical coupling to yield both of homo- and cross-coupling reactions. The radical species have enough reactivity to promote the coupling

reactions, and thus the contribution of metal catalyst would not be observed. These reactions are two-photon processes. In contrast, the cyanomethylation of benzene, which was proceeded via addition-elimination reaction with one photon, required the metal catalysis by the Pd nanoparticles, which was evidenced by the Arrhenius plot and the reaction test with the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Considering from the results of the cyanomethylation of aliphatic and aromatic hydrocarbons, it was revealed that the Pd catalyst activates the aromatic ring to react with cyanomethyl radical. In conclusion, the Pd catalyst is important for the photocatalytic addition-elimination reaction involving the reaction between aromatic ring and less active radicals such as cyanomethyl radical.

In chapter 6, the lactonization from diols was examined with Pt/TiO<sub>2</sub> photocatalysts. The reaction from 1,2-benzenedimethanol to phthalide was well promoted by Pt loaded rutile TiO<sub>2</sub> photocatalyst. The obtained amount of phthalide was up to 90 % in yield with 90 % in selectivity because rutile TiO<sub>2</sub> photocatalyst could not enhance successive oxidation of phthalide. In order to expand the scope of this reaction, some diols were also examined over the Pt/TiO<sub>2</sub> photocatalysts, and found that all examined reactions proceeded in the presence of Pt loaded rutile TiO<sub>2</sub> photocatalyst more than Pt loaded anatase TiO<sub>2</sub> photocatalyst. In addition, it is proposed that the combination of acid catalyst and Pt/TiO<sub>2</sub> photocatalyst will improve the reaction rate of the lactonization.

Chapter 7 summarizes the thesis. Through Chapters 2–4, the reaction mechanism on the protonated titanate nanotube as a Lewis acid catalyst was clarified, and the catalytic performance was improved by adding Nb species. In Chapters 5 and 6, photocatalytic organic reactions were developed by using typical photocatalysts, and it was proposed that combination of a metal catalyst and acid catalyst would be improved photocatalytic performance.