Synthesis of Titanosilicate Zeolite from Bulk Titania via Mechanochemical Route

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An easy and highly reproducible synthesis method for titanosilicate zeolites has been developed, which can use bulk titania and silica as source materials. In this method, a uniform silica–titania composite is prepared from titania and silica powders by the solid-phase mechanochemical reaction and converted into a titanosilicate zeolite by the succeeding hydrothermal treatment.

Titanosilicate zeolites such as TS-1,[1] Ti-Beta,[2] and Ti-MWW[3] are attracting much attention, since they exhibit remarkably high catalytic activities in the oxidation of various organic compounds using hydrogen peroxide as an oxidant.[4] Because the catalytically active sites of titanosilicates are tetrahedrally-coordinated Ti atoms isostructurally substituted for framework Si atoms,[4] it is crucial to incorporate tetrahedrally-coordinated Ti atoms dispersedly into a silica matrix in the synthesis of titanosilicate materials. Conventional synthesis methods therefore usually employ expensive titanium and silica alkoxides as source materials, which are hydrolyzed and copolymerized in aqueous medium to form a hydrogel mixture. However, due to the difference in the hydrolysis rates of titanium and silicon alkoxides, it is difficult to obtain a uniformly mixed silica–titania precursor without careful manipulation in the gel preparation step; tiatnium species are often aggregated separately to become catalytically inactive octahedrally-coordinated Ti species.

In this work, we have developed a new synthesis route to titanosilicate materials by utilizing mechanochemical reaction, which has been used for the synthesis of composite materials[5] or the degradation of harmful compounds.[6] In this novel route, inexpensive bulk titania and silica can be employed as source materials. These source materials are first ground by using a planetary ball mill at autogenous temperature and mixed at the atomic level in the solid phase to produce a uniform silica–titania composite by the mechanochemical reaction. Thus, synthesized precursor is crystallized into an MFI-type titanosilicate TS-1 by the succeeding hydrothermal treatment in the presence of tetrapropylammonium hydroxide (TPAOH), a typical structure-directing agent for an MFI-type zeolite. This simple synthesis method does not require practiced operation to give a nanocomposite from a bulk material, so it enables the easy and highly reproducible synthesis of titanosilicates as well as reduces the material cost for the synthesis of titanosilicate zeolites.

The XRD patterns and the UV–vis spectra of the materials obtained in the course of this new mechanochemical route are shown in Figures 1 and 2, respectively. The starting mixture of anatase-type titania powder (Wako) and fumed silica (Aerosil200, Nippon Aerosil) with the SiO_2/TiO_2 molar ratio of 50 shows diffraction peaks and an absorption band typical of anatase-type titania. In contrast, after the grinding at 700 rpm for 36 h using a planetary ball mill, the diffraction peaks

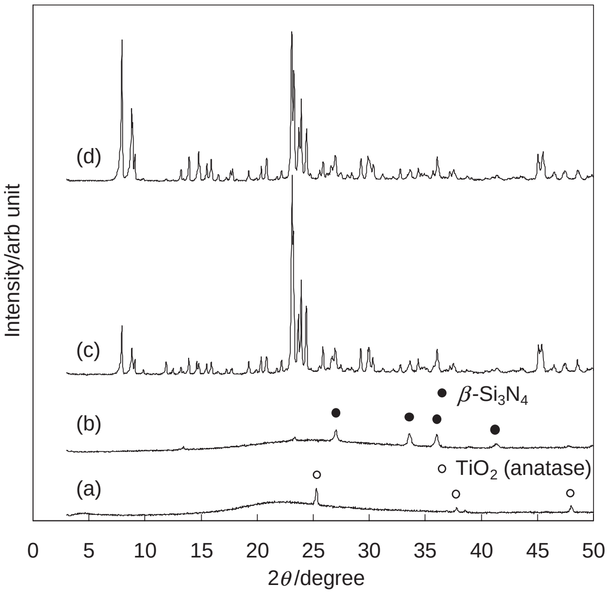

Figure 1. XRD patterns of the products obtained in the course of the mechanochemical path. (a) Mixture of fumed silica and anatase-type titania, (b) after the grinding at 700 rpm for 36 h, (c) after the hydrothermal treatment in the presence of TPAOH, and (d) after the calcination.

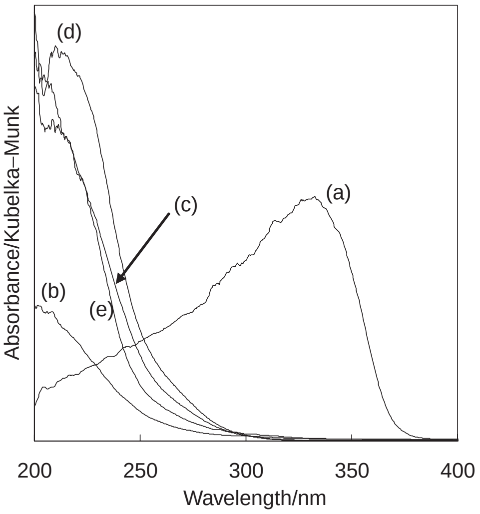

Figure 2. UV–vis spectra of the products obtained in the course of the mechanochemical path. (a) Mixture of fumed silica and anatase-type titania, (b) after the grinding at 700 rpm for 36 h, (c) after the hydrothermal treatment in the presence of TPAOH, (d) after the calcination, and (e) TS-1c synthesized by the conventional method.

Table 1. Physical and catalytic properties of TS-1 materials

	Si/Ti	A_{Lang}[a] /$\mathrm{m^2 \cdot g^{-1}}$	V_{m}[b] /$\mathrm{cm^3 \cdot g^{-1}}$	Primary particle size /μm	Conversion[c,d] /mol %	TON[c,e]	Selectivity/mol %[c]		
							epoxide	diol	others[f]
TS-1m	84	484	0.114	≈ 2	9.8	31	94.0	2.3	3.7
TS-1c	85	561	0.129	≈ 2	9.8	31	97.2	2.8	0.0

[a]Langmuir surface area and [b]micropore volume based on the Langmuir plot of N_2 adsorption isotherm at −196 °C. [c]1-Hexene: 10 mmol, hydrogen peroxide: 3 mmol, catalyst: 50 mg, acetonitrile: 5 mL, 60 °C, 3 h. [d]Oxidant-based conversion. [e]mol-(epoxide+diol)/mol-Ti. [f]Decomposition products.

derived from the anatase structure disappear, indicating the complete degradation of the crystalline structure of titania and the formation of an amorphous material. Small diffraction peaks at 27.1, 33.7, and 36.1° are assignable to β-$\mathrm{Si_3N_4}$ derived from the milling pot and balls. The UV–vis absorption band, which is observed around 340 nm before the grinding (Figure 2a), is drastically shifted to the lower wavelength after the grinding (Figure 2b), indicating that the coordination of Ti species has changed from octahedral to tetrahedral. These findings in XRD patterns and UV–vis spectra suggest that the grinding causes the mechanochemical reaction to degrade the crystalline structure of titania and to incorporate isolated tetrahedral Ti species into amorphous silica matrix.

When thus prepared silica–titania composite is hydrothermally treated at 170 °C in the presence of TPAOH, the product exhibits diffraction peaks characteristic of the MFI-type structure (Figure 1c). The presence of UV–vis absorption band at around 210 nm demonstrates the preservation of tetrahedrally-coordinated Ti species in this MFI-type product, proving the successful formation of a TS-1 material. The calcined final product, designated here TS-1m, shows practically the same diffraction pattern and UV–vis absorption spectrum. It is worth noting that a TS-1 material is also obtained when a mixture of the ground silica–titania composite and TPAOH powder is heat-treated in a steam atmosphere.[7,8] In this case, this TS-1 material is obtained by the solid-phase reaction all through the synthesis procedure from the source materials to the final product.

Table 1 summarizes the physical properties of TS-1m compared with those of TS-1c, a TS-1 material prepared by the conventional method.[1] Because of the commingling of silicon nitride described above, the Si/Ti ratio of TS-1m is larger than that of initial silica–titania mixture. Its high specific surface area and large micropore volume clearly demonstrate the porous structure of TS-1m, although these values are somewhat smaller than those of TS-1c presumably due to the concomitance of non-porous silicon nitride. The SEM observation reveals that both TS-1 materials have primary particle sizes of ca. 2 μm and a coffin-like particle shape characteristic of an MFI-type zeolite material.

The catalytic activity of TS-1m in the oxidation of 1-hexene employing hydrogen peroxide as an oxidant is also exhibited in Table 1. TS-1m shows a high catalytic performance in terms of the high turnover number (TON) to epoxide and diol and the good selectivity to epoxide, which are comparative to those of TS-1c. It is to be noted that the silica–titania composite just ground without the hydrothermal treatment shows no activity as an epoxidation catalyst, although it has tetrahedrally-coordinated Ti species (Figure 2b). This should be attributed to its high surface hydrophilicity; the active sites would be poisoned by water molecules in the reaction system.[9] This is evidenced by the fact that the catalytic activity appears when its surface hydrophobicity is improved by the trimethylsilylation.[10] These findings strongly indicate that Ti species in the ground composite are not left separately from zeolite but incorporated into the framework of zeolite, whose surface is far hydrophobic than that of ground powder.

In conclusion, titanosilicate zeolites have been successfully synthesized from bulk titania and silica through the newly developed route using mechanochemical reaction. As far as we know, this is the first report on the successful synthesis of titanosilicate zeolites using bulk titania as a Ti source. This simple and highly reproducible method would be applicable to the synthesis of other types of microporous and mesoporous titanosilicates as well as to the solid-phase synthesis of various nanocomposites from component bulk materials.

K. Y. thanks Dr. J. Kano at Tohoku University for meaningful discussion on mechanochemical reactions and Nippon Aerosil Co., Ltd. for the supply of fumed silica products.

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