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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Synthesis of Ti-Beta via mechanochemical route

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Abstract A *BEA-type titanosilicate, Ti-Beta, has been synthesized by a new method using mechanochemical reaction. In this new synthesis method, titania and silica powders are used as source materials and ground by using a planetary ball mill. Thus obtained silica–titania composite is hydrothermally treated in the presence of tetraethylammonium fluoride as a structure-directing agent to obtain a Ti-Beta material. The titanosilicate samples obtained are characterized by powder X-ray diffractometry and UV–visible spectroscopy. The crystallization behaviors and the catalytic activities of Ti-Beta materials synthesized by this new method are compared with those synthesized conventionally from silicon and titanium alkoxides.

Introduction

Titanosilicate zeolites are important catalysts because they exhibit high catalytic activities in various oxidation reactions using hydrogen peroxide as an oxidant [1, 2]. In particular, TS-1 [3] is known to be an excellent catalyst for the oxidations of linear alkenes or alkanes [3, 4] and has been recently applied as an industrial catalyst to obtain propylene oxide from propylene. However, the MFI-type framework of TS-1 has only 10-membered ring micropores [5], which limits the availability of reactants; bulky reactants with the molecular sizes larger than the micropore openings of MFI-type framework (0.51–0.56 nm) cannot access catalytically active centers inside the micropores. For bulkier reactant molecules, therefore, titanosilicate zeolites having larger pore openings should be employed.

In this regard, the *BEA-type zeolite framework [5] would be a good candidate as a catalyst for bulky reactant molecules. The *BEA-type framework has 12-membered ring large pore openings sizing at ca. 0.67 nm, which is larger than that of TS-1. Actually, a *BEA-type titanosilicate, Ti-Beta, has expanded the application area of titanosilicate zeolites as an oxidation catalyst for bulky organic compounds such as cyclohexene and cyclooctene [6–14].

We have already reported the development of a new synthesis method for TS-1 utilizing mechanochemical reaction [15–17]. This mechanochemical synthesis method employs titania and silica powders as starting materials, which are allowed to react mechanochemically to be a silica–titania composite as a precursor to TS-1. Figure 1 illustrates the precursor preparation process using the mechanochemical reaction occurring at the grinding using a planetary ball mill. By the rotation and the revolution of a milling pot, balls installed inside the pot hit each other to produce powerful impact and/or friction energy according to operational conditions, such as the milling time and the disk rotation speed [18]. This mechanical energy promotes the degradation of crystalline structure, the cleavage of bonds, and the formation of new bonds between silicon and titanium species, resulting in the formation of a uniform silica–titania mixture. Thus prepared silica–titania mixture is hydrothermally treated in the presence of organic structure-directing agent (SDA) to be crystallized into TS-1 materials.

In this work, our novel method is applied to the synthesis of a Ti-Beta material. In the conventional synthesis method of Ti-Beta, silicon, and titanium alkoxides, which

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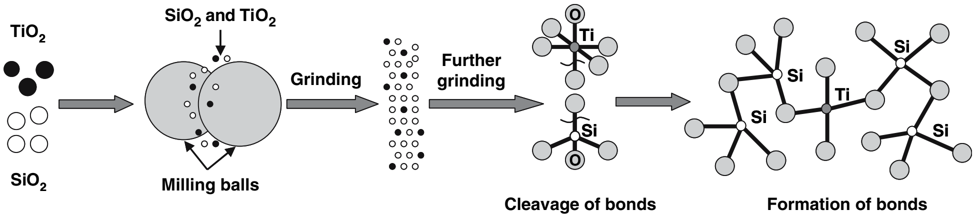

Fig. 1 Schematic illustration of the precursor preparation via the mechanochemical process

are rather expensive materials, are employed as precursors, which are copolymerized under the careful control of their hydrolysis rates to be a uniform precursor gel. In contrast, the mechanochemical synthesis method would obtain a Ti-Beta material from inexpensive bulk materials without skilled manipulation.

Experimental

Precursor preparation by mechanochemical reaction

Ultrafine powder of anatase-type titania ST01 (Ishihara Industry) and fumed silica Aerosil 200 (Nippon Aerosil) were used as titanium and silicon sources, respectively. Typically, 0.027 g of titania and 1.0 g of silica were mixed (Si/Ti molar ratio = 50) and ground by using a Fritsch P-7 planetary ball mill equipped with a milling pot and balls made of silicon nitride. The inside diameter of the milling pot was 40 mm, and seven balls with a diameter of 15 mm were charged in each pot. The materials were ground in a cycle of 15-min-milling and 15-min-pause.

Hydrothermal synthesis of Ti-Beta

Ti-Beta materials were synthesized from a silica–titania composite obtained above as silicon and titanium sources. To this silica–titania composite added were aqueous solutions of tetraethylammonium hydroxide (Wako) and hydrofluoric acid (Wako). The suspension was stirred and heated to evaporate excess water to obtain a mother mixture with the molar composition of SiO_2:0.02 TiO_2:0.55 tetraethylammonium fluoride (TEAF):7.63 H_2O [12, 13]. This was hydrothermally treated in a stainless autoclave at 150 °C for 8 days under static conditions. The products obtained were washed, filtered, dried at room temperature and calcined at 540 °C for 8 h.

For a control, a Ti-Beta material was synthesized conventionally from tetraethyl orthosilicate (TEOS, TCI) and tetrabutyl orthotitanate (TBOT, TCI) according to the literatures [11, 12]. The molar composition of the mother gel and hydrothermal treatment and calcination conditions were the same as mentioned above.

Characterization

The powder X-ray diffraction (XRD) patterns were collected with a Rigaku Type RAD-IC diffractometer with a Cu $K\alpha$ irradiation (40 kV, 20 mA). The diffuse reflectance UV–visible spectra were obtained with a Shimadzu UV-2550 spectrometer.

Catalytic reaction

Ti-Beta materials were used as catalysts in the oxidation of cyclohexene by using hydrogen peroxide as an oxidant. A total of 10 mmol of cyclohexene, 3 mmol of hydrogen peroxide (Santoku Chemicals, 31.4 wt.% aqueous solution), 0.05 g of a catalyst, and 5 mL of acetone (Wako) as a solvent were mixed in a 10 mL flask and allowed to react at 60 °C for 3 h under vigorous stirring. The products collected were analyzed with a Shimadzu GC-14B gas chromatograph equipped with a J&W Scientific DB-WAX capillary column and a flame ionization detector.

Results and discussion

Properties of the products obtained through mechanochemical route

The XRD patterns and the UV–visible spectra of the products obtained along the mechanochemical synthesis route are shown in Figs. 2 and 3, respectively. After the grinding for 36 h with a planetary ball mill, the diffraction peaks assignable to anatase-type titania disappear to show the degradation of crystalline structure of titania (Fig. 2b). On the other hand, small diffraction peaks assignable to β-Si_3N_4, derived from the milling media, are observed. Its UV–visible spectrum (Fig. 3b) shows that the absorption band is shifted from 340 to 210 nm by the grinding, demonstrating the change in Ti coordination from tetrahedral to octahedral [2]. These findings suggest that titania and silica are allowed to react mechanochemically during the grinding to form a uniformly mixed amorphous composite having tetrahedrally coordinated Ti species.

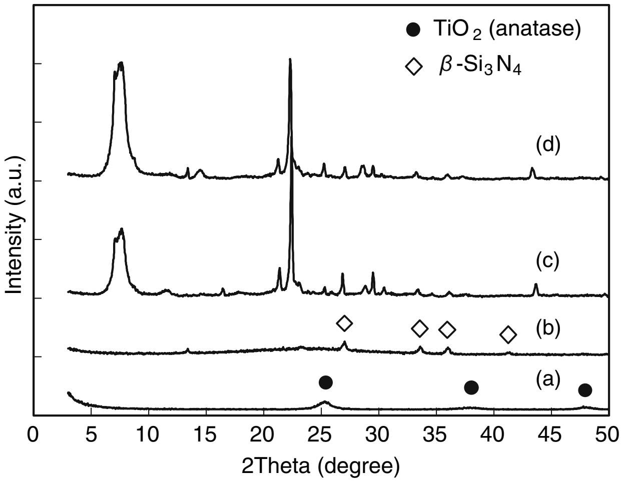

Fig. 2 XRD patterns of the products obtained along the mechanochemical synthesis method; (a) before and (b) after the mechanochemical reaction, (c) after the hydrothermal synthesis, and (d) after the calcination

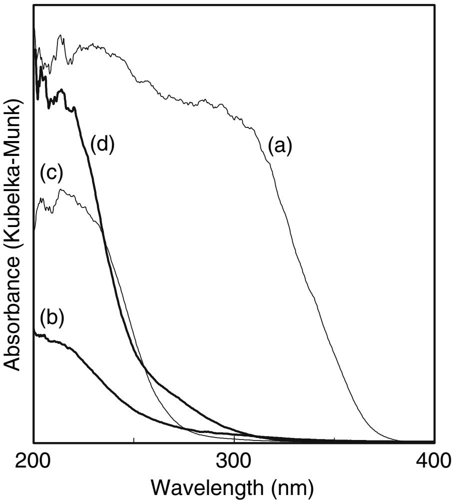

Fig. 3 UV–visible spectra of the products obtained along the mechanochemical synthesis method; (a) before and (b) after the mechanochemical reaction, (c) after the hydrothermal synthesis, and (d) after the calcination

When thus prepared silica–titania composite is hydrothermally treated at 150 °C in the presence of TEAF as SDA, the product shows diffraction peaks characteristic of the *BEA-type zeolite structure (Fig. 2c). The UV–visible spectrum of this zeolitic material also shows the absorption band at 210 nm, indicating the presence of tetrahedrally coordinated Ti species. The diffraction pattern and the UV–visible spectrum practically do not change after the calcination. Although the syntheses by other synthesis methods using no fluoride anions [10, 13] are also attempted, *BEA-type materials have not been obtained so far.

When titania and silica are ground in a milling media made of zirconia, the ground composite is crystallized into a *BEA-type zeolite (Fig. 4b) under the same hydrothermal treatment conditions. Presumably, the contamination of zirconia from the milling media [16] would disturb the nucleation of *BEA-type zeolite. Even in this case, however, a *BEA-type product can be obtained when the silica–titania composite is mixed with pure silica (Fig. 4c), which would facilitate the nucleation of *BEA structure during the hydrothermal synthesis.

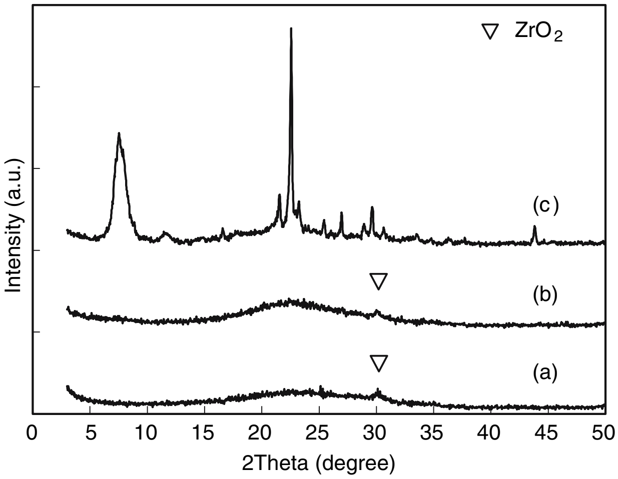

Fig. 4 XRD patterns of the products obtained from a mechanochemically reacted silica–titania composite ground in milling media made of zirconia; (a) before and (b) after the hydrothermal treatment and (c) after hydrothermally treating a mixture of silica and a mechanochemically reacted silica–titania composite

Crystallization behaviors

Figure 5 compares the XRD patterns of the products obtained from TEOS and TBOT and from the mechanochemically reacted silica–titania composite after various hydrothermal treatment time. In the conventional synthesis using TEOS and TBOT (Fig. 5a), *BEA-type zeolite phase is observed after 8 days of hydrothermal treatment. On the other hand, when the mechanochemically reacted silica–titania composite is employed as a silicon and titanium sources and hydrothermally treated under the same conditions (Fig. 5b), the *BEA phase is obtained within 4 days. The presence of small building units in the ground silica–titania composite can be a reason for this shorter crystallization time. The nuclei of zeolite are created from small secondary building units [5] such as double 4-membered ring or 6-membered ring. Although the ground silica–titania composite has macroscopically an amorphous structure, tiny building units, which cannot be detected by the XRD measurement, might remain or be formed during the mechanochemical reaction process to accelerate the crystallization of *BEA-type zeolites.

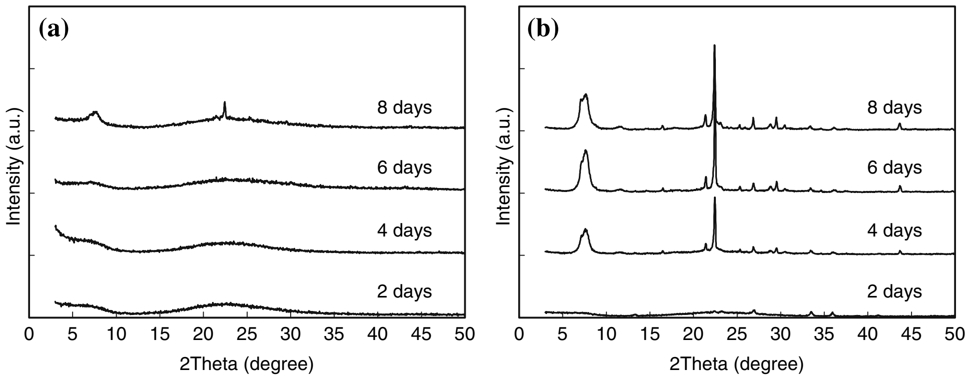

Fig. 5 XRD patterns of the products obtained from (**a**) tetraethyl orthosilicate and tetrabutyl orthotitanate and (**b**) a mechanochemically reacted silica–titania composite with various synthesis time

The crystallization time is further shortened when the water content of the starting mixture is smaller. Figure 6 shows the XRD patterns of the product synthesized from the mixture using less amount of water ($H_2O/SiO_2 = 4.21$ instead of 7.63). It clearly indicates that a *BEA-type material is obtained after 2 days of hydrothermal treatment. In this case using less amount of water, the higher concentrations of silica and titania would make the nucleation of the *BEA-type zeolite faster, which leads to the shorter crystallization time.

Catalytic activities of Ti-Beta materials

Table 1 exhibits the catalytic activities of Ti-Beta materials prepared through the conventional and mechanochemical routes. All the materials contain smaller amounts of Ti species than their mother mixtures, as usually observed for Ti-Beta synthesized in the presence of fluoride anions [12]. For Ti-Beta materials synthesized from silica–titania composite obtained by using silicon nitride milling media, the Si/Ti ratios are furthermore larger owing to the commingling of silicon nitride.

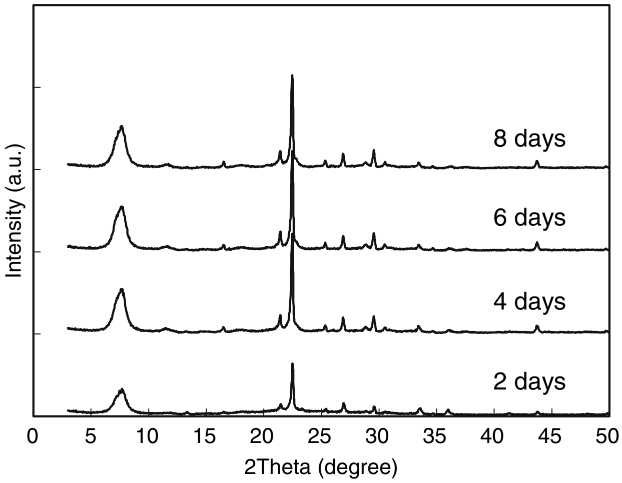

Fig. 6 XRD patterns of the products obtained from a mechanochemically reacted silica–titania composite in the presence of a smaller amount of water ($H_2O/SiO_2 = 4.21$)

Ti-Beta synthesized from the silica–titania composite shows high catalytic activity in terms of the conversion of cyclohexene; the turnover number to epoxide and diol is higher than that of the conventional Ti-Beta material synthesized from TEOS and TBOT, although the conversion is lower. It is to be noted that the selectivity to allylic oxidation products is lower for this catalyst. As described above, the silica–titania composite is crystallized rapidly compared with the mother gel prepared from TEOS and TBOT. Therefore, after 8 days of hydrothermal synthesis, Ti-Beta synthesized from the silica–titania composite would contain less structural defects that catalyze the allylic oxidation.

The catalytic activity is improved when Ti-Beta is synthesized from the silica–titania composite at higher hydrothermal treatment temperature, 170 °C. The catalytically active center of Ti-Beta is tetrahedrally coordinated Ti species dispersedly incorporated into the framework. Although the UV–visible spectrum of ground silica–titania composite (Fig. 3b) shows that Ti species have tetrahedral coordination, some of them might not be dispersed as monomer species. By the succeeding hydrothermal treatment at a higher temperature, Ti species would be completely dissolved into a monomer species to be incorporated dispersedly into the framework of a Ti-Beta, resulting in the formation of highly active Ti-Beta catalyst.

On the other hand, the Ti-Beta material synthesized from the silica–titania composite ground in zirconia milling media shows far less catalytic activity. Because this silica–titania composite contains zirconia derived from the milling media as an impurity, Zr species incorporated as framework atoms or as extraframework cations during the hydrothermal synthesis would spoil their catalytic activity. At the same time, the selectivity to the allylic oxidation products is remarkably high for this catalyst. This would also be caused by the concomitant zirconia, which is evidenced by the finding that zirconia catalyzes

Table 1 Catalytic activities of Ti-Beta materials in the oxidation of cyclohexene

Si and Ti sources	Si/Ti	Si/Zr	Conversion[a] (mol %)	TON[b]	Selectivity (mol%)		
					Epoxide	Diol	Others[c]
TEOS and TBOT	131	–	14.8	50	52.4	17.4	30.2
SiO_2–TiO_2 (Si_3N_4)[d]	314	–	7.8	82	39.9	52.9	7.2
SiO_2–TiO_2 (Si_3N_4)[d,e]	530	–	14.3	266	53.3	39.9	6.9
SiO_2–TiO_2 (ZrO_2)[f]	131	122	2.5	3	10.8	16.5	72.7

Catalytic reaction conditions: catalyst 0.05 g, cyclohexene 10 mmol, hydrogen peroxide 3 mmol, acetone 5 mL, 60°C, 3 h

[a] Oxidant-based conversion

[b] Turnover number to epoxide and diol (mol-(epoxide + diol)/mol-Ti)

[c] 2-cyclohexene-1-one and 2-cyclohexene-1-ol

[d] Silica–titania composite obtained by using silicon nitiride milling media

[e] Hydrothermally synthesized at 170 °C

[f] Silica–titania composite obtained by using zirconia milling media

the allylic oxidation of cyclohexene under the same reaction conditions.

Conclusion

Silica–titania composite is prepared by the mechanochemical reaction of bulk silica and titania and crystallized into a *BEA-type zeolite through the hydrothermal treatment. By using this silica–titania composite as a silicon and titanium sources, the crystallization time to *BEA-type titanosilicate can be greatly shortened. Thus obtained Ti-Beta material shows high catalytic activity in the oxidation of cyclohexene using hydrogen peroxide as an oxidant. The contamination of zirconia from a milling media into a silica–titania composite not only disturbs the crystallization of the *BEA-type structure, but also depresses the catalytic activity of the final Ti-Beta product.

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