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Titanosilicate Zeolite Synthesized via Mechanochemical Route

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MFI-type titanosilicate zeolite TS-1 is synthesized via a newly developed mechanochemical route, and the effects of mechanochemical reaction conditions on the physical and chemical properties are investigated. In the mechanochemical route, titania and silica powders are ground by using a planetary ball mill to yield a silica-titania composite powder, which is converted into TS-1 through hydrothermal treatment. TS-1 samples are characterized by powder X-ray diffractometry and UV-visible spectroscopy, and their catalytic activities in the alkene oxidation reaction are evaluated. Several parameters of the mechanochemical reaction such as the disk rotation speed, the grinding time, and the molar ratio of silica and titania are changed to evaluate their effects on the properties of resulting materials. It is demonstrated that these parameters have significant effects on the physical and chemical properties of the final product.

Keywords

Titanosilicate, Mechanochemical reaction, Planetary ball mill, Zeolite catalyst, TS-1

1. Introduction

Titanosilicate zeolites^{1)~6)} are catalysts with extremely high activities for several oxidation reactions, such as the oxidation of alkenes, alkanes, and aromatic compounds and the ammoximation of ketones using hydrogen peroxide as the oxidant. Recently, an MFI-type titanosilicate catalyst TS-1 has been industrially applied.

Titanosilicate zeolites contain tetrahedrally-coordinated Ti atoms, which are isostructurally substituted for Si atoms to act as the catalytically active centers^{7)~9)}. For the successful incorporation of Ti atoms into the silicate framework, a titanium alkoxide monomer is used as the Ti source, which is co-polymerized with a silicon alkoxide. However, this procedure has disadvantages such as the high cost of source materials and the necessity for careful control of the hydrolysis rates to prevent the formation of extra-framework titania species. To overcome these problems, we have developed an easy and highly reproducible synthesis route for titanosilicate materials based on mechanochemical reaction¹⁰⁾.

Mechanochemical reaction can be defined as chemical reaction caused by the friction and/or the impact energy produced during the grinding^{11),12)}. When materials are ground in a planetary ball mill, not only their

physical properties such as the particle size and the crystalline structure but also their chemical properties are changed by the mechanochemical reaction^{13)~19)}. We have utilized this reaction in the preparation of a precursor for a titanosilicate material. Through the mechanochemical reaction of bulk titania and silica, uniformly mixed silica-titania composite is obtained¹⁰⁾. By hydrothermally treating this mechanochemically reacted silica-titania composite, a TS-1 material is obtained inexpensively, easily, and highly reproducibly.

The present study investigates the effects of the mechanochemical reaction conditions on the physical and chemical properties of TS-1 materials. **Figure 1** illustrates the movement of a planetary ball mill together with several operational conditions involved in the mechanochemical reaction. Each milling parameter would affect the chemical and physical properties of the resulting mixtures and final TS-1 materials. For example, the disk rotation speed affects the rate of mechanochemical reaction and the amount of impurities introduced from pots and balls because of the close relationship with the force applied by the milling media to the loaded materials. A similar effect can be expected for the total milling time. The size and the structure of source materials could also affect the rate of mechanochemical reaction. This investigation identifies the optimum milling conditions to obtain a highly active TS-1 catalyst.

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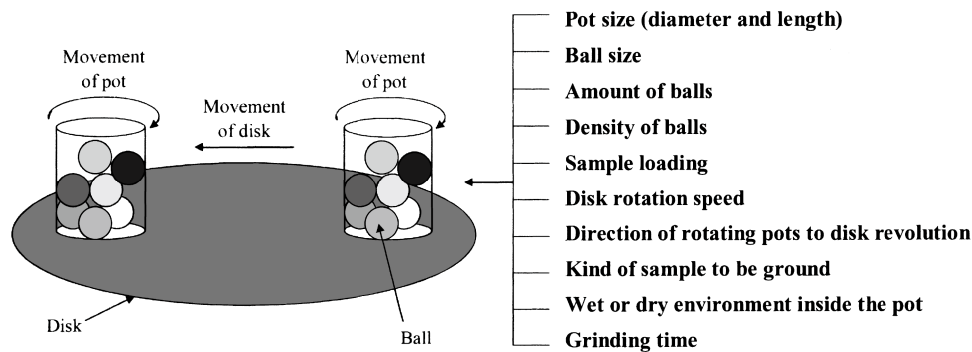


Fig. 1 Illustration of a Planetary Ball Mill and Operational Conditions of Mechanochemical Reactions

2. Experimental

2.1. Mechanochemical Reaction

As titanium sources, three types of anatase-type titania were obtained from Ishihara Ind. (ST01), Merck (TiO₂m) and Wako (TiO₂w). The particle sizes of these three samples estimated by a transmission electron microscope (TEM) were *ca.* 20, 100-200 and 100-200 nm, respectively. As silicon sources, fumed silica Aerosil 200 (Nippon Aerosil) with an amorphous structure or precipitated silica (Wako) with a crystalline α -quartz structure were used. Titania and silica powders were mixed at a Si/Ti molar ratio of 20 and ground by using a Fritsch P-7 planetary ball mill equipped with a zirconia pot and balls. The mixture was ground in a cycle of 15-min-milling and 15-min-pause times. Here, the grinding time indicates the total of milling and pause times. The inside diameter of the milling pot was 40 mm, and 7 balls with a diameter of 15 mm were charged in each pot. Several operational conditions, such as the total milling time, the disk rotation speed, and the molar ratio of the starting mixture, were varied.

2.2. Hydrothermal Synthesis of TS-1

The mechanochemically reacted silica-titania composite and fumed silica Aerosil 200 added to adjust the Si/Ti molar ratio to 50 were suspended in an aqueous solution of tetrapropylammonium hydroxide (TPAOH, Tokyo Chemical Ind. Co.) as a structure-directing agent. The resulting suspension with the chemical composition of SiO₂ : 0.2 TiO₂ : 0.4 TPAOH : 20 H₂O was hydrothermally treated in a stainless steel autoclave at 170°C for 5 days with continuous stirring. The product was washed, centrifuged, dried at room temperature, and calcined at 540°C for 8 h.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns were observed with a Rigaku Type RAD-IC diffractometer with a Cu K α irradiation (40 kV and 20 mA). The diffuse reflectance UV-visible spectra were obtained with a Shimadzu UV-2550 spectrophotometer. The chemical compositions of the materials were measured

with a Parkin-Elmer Optima 3300SYS inductively coupled plasma atomic emission (ICP) spectrometer.

2.4. Catalytic Reaction

The synthesized TS-1 catalysts were evaluated for the oxidation of 1-hexene using hydrogen peroxide as the oxidant. TS-1 samples were washed with hydrochloric acid before the catalytic reaction to remove ion-exchangeable impurities, which might spoil the catalytic activity of the framework Ti species²⁰. 0.05 g of washed catalyst was mixed with 10 mmol of 1-hexene (Wako), 3 mmol of hydrogen peroxide (31.4 wt% aqueous solution, Santoku Chemicals) and 5 ml of acetone (Wako) as a solvent in a 10 ml flask and allowed to react at 60°C for 3 h with vigorous stirring. The products collected were analyzed with a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and a J&W Scientific DB-WAX capillary column.

3. Results and Discussion

3.1. Effect of Si and Ti Sources

Figures 2 and 3 show the XRD patterns and the UV-visible spectra of the silica-titania composites obtained from various silicon and titanium sources after the milling at 600 rpm for 24 h. As reported previously¹⁰, the diffraction peaks assignable to anatase-type titania disappear after milling (Fig. 2), although the crystalline silica structure is slightly retained for the mixture of precipitated silica and ST01 (Fig. 2 (d)). Small broad peaks around 30.2° and 34.6° observed in all samples are assigned to zirconia derived from the milling pot and balls.

The UV-visible spectra of all composites (Fig. 3) show absorption bands around 210 nm attributed to tetrahedral Ti species, indicating the coordination change from octahedral to tetrahedral caused by the mechanochemical reaction. However, the spectra of the mixtures prepared from TiO₂m or TiO₂w with larger particle sizes (Fig. 3 (a), (b)) include a slight absorption peaks around 330 nm assignable to the octahedral Ti species (Fig. 3 (a), (b)). Similarly, the spectrum of

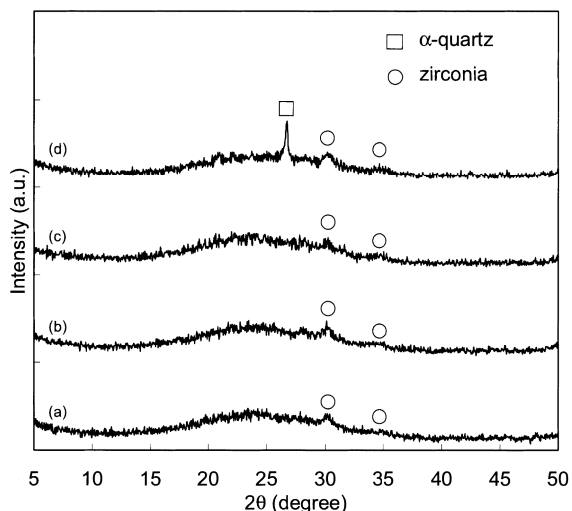


Fig. 2 XRD Patterns of Ground Silica-titania Mixtures Prepared from (a) Fumed Silica and TiO_2m , (b) Fumed Silica and TiO_2w , (c) Fumed Silica and ST01, and (d) Precipitated Silica and ST01

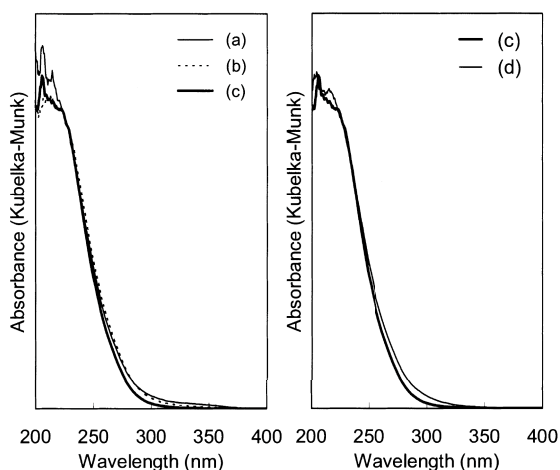


Fig. 3 UV-visible Spectra of Ground Silica-titania Mixtures Prepared from (a) Fumed Silica and TiO_2m , (b) Fumed Silica and TiO_2w , (c) Fumed Silica and ST01, and (d) Precipitated Silica and ST01

the mixture of precipitated silica and ST01 (**Fig. 3** (d)) contains a small absorption band in this region. These findings indicate that the particle size and the structure of the starting materials have important effects on the resultant mixture; mechanochemical reaction starting from large particles and/or from solid crystalline particles would take longer to obtain well mixed silica-titania composite. Therefore, the following experiments use fumed silica and ST01 as the starting materials.

3.2. Effect of Milling Media

Figure 4 shows the UV-visible spectra of the mixture of fumed silica and ST01 ground at 600 rpm for

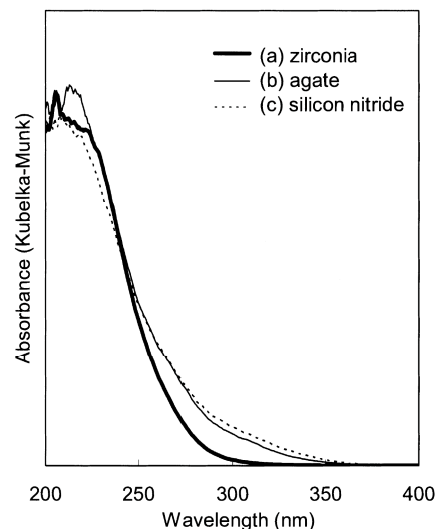


Fig. 4 UV-visible Spectra of Silica-titania Mixtures Ground in (a) Zirconia, (b) Agate, and (c) Silicon Nitride Pot

24 h in different milling media (milling pot and balls). Only the absorption band of tetrahedral Ti species at around 210 nm is observed if the mixture is ground in zirconia media. On the other hand, slight absorption of the octahedral Ti species is also observed around 330 nm if the mixture is ground in agate or silicon nitride media.

The impact energy becomes higher with increasing ball weight, so higher density balls can produce larger impact energy^{4),5)}. The density of zirconia is 6.07 g/cm^3 , which is far higher than those of silicon nitride and agate, 3.21 and 2.64 g/cm^3 , respectively. Therefore, the grinding in zirconia media effectively degrades the titania structure and mixes the silica and titania uniformly through mechanochemical reaction. Therefore, the following experiments use a zirconia pot and balls as the milling media.

3.3. Effect of Si/Ti Molar Ratio

Figure 5 shows the UV-visible spectra of silica-titania mixtures with various Si/Ti ratios after the milling at 600 rpm for 24 h. The mixtures consist of 0.03 mol fumed silica and various amounts of ST01. The mixture with a Si/Ti molar ratio of 5 shows a large absorption around 330 nm (**Fig. 5** (a)), suggesting preservation of the octahedral Ti species. This absorption decreases with increasing Si/Ti ratio. Apparently Ti atoms are completely converted into tetrahedrally-coordinated species and incorporated into the silica matrix with Si/Ti ratio larger than 20 under these milling conditions.

The XRD patterns of the final TS-1 products synthesized from the silica-titania composite obtained above are exhibited in **Fig. 6**. The Si/Ti ratio of the mother gel is adjusted to 50 by adding fumed silica to the silica-titania composite. Amorphous material is ob-

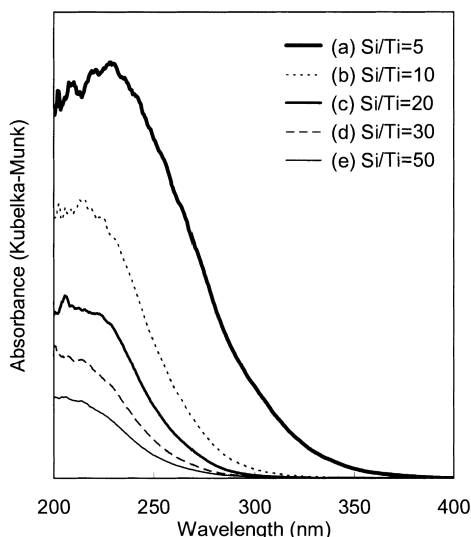


Fig. 5 UV-visible Spectra of Ground Silica-titania Mixtures with Si/Ti Ratios of (a) 5, (b) 10, (c) 20, (d) 30, and (e) 50

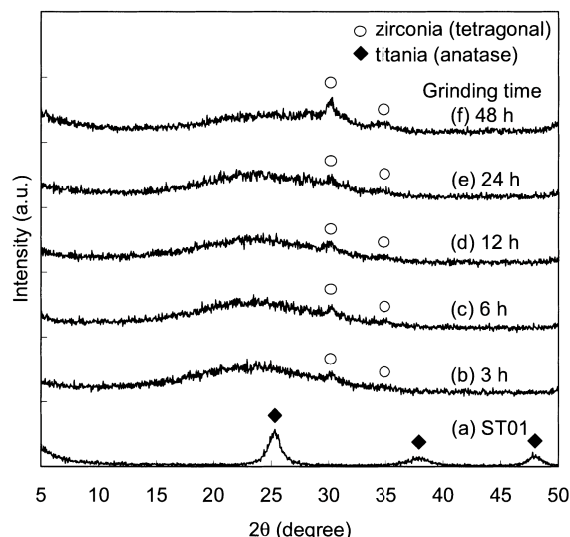


Fig. 7 XRD Patterns of (a) ST01 and Silica-titania Mixtures Ground for (b) 3 h, (c) 6 h, (d) 12 h, (e) 24 h, (f) 48 h

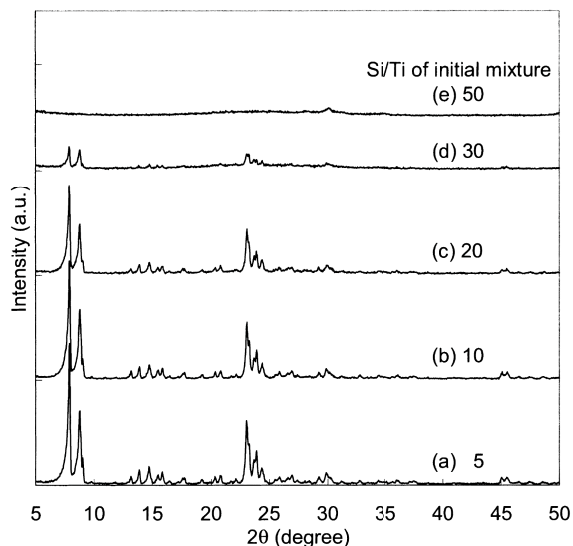


Fig. 6 XRD Patterns of TS-1 Materials Synthesized from Ground Silica-titania Mixtures with Si/Ti Ratios of (a) 5, (b) 10, (c) 20, (d) 30, and (e) 50

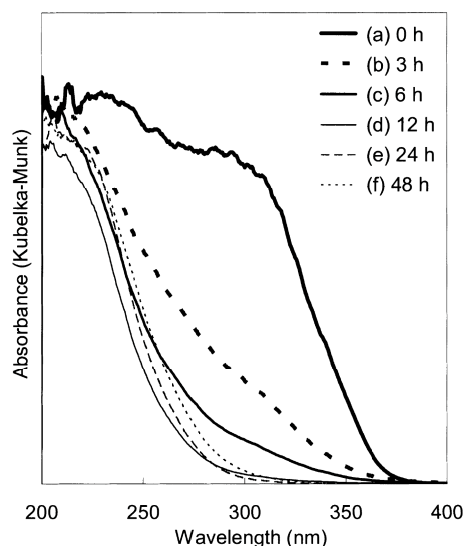


Fig. 8 UV-visible Spectra of Silica-titania Mixtures Ground for (a) 0 h, (b) 3 h, (c) 6 h, (d) 12 h, (e) 24 h, (f) 48 h

tained from a silica-titania mixture with Si/Ti molar ratio of 50 by grinding and hydrothermal treatment, if fumed silica is not added at the hydrothermal synthesis stage (Fig. 6 (e)). Considering that silica-titania composite ground in an agate or a silicon nitride pot can be crystallized into an MFI-type zeolite without adding fumed silica, the concomitant zirconia impurity must hinder the nucleation of the MFI phase. In contrast, crystalline TS-1 materials are obtained if fumed silica is added at the hydrothermal synthesis stage. In these cases, the added fumed silica provides nuclei for the MFI phase and growing crystals incorporate the silica-titania composite. Consequently, if zirconia is

used for the milling media, the mixture should be ground with the Si/Ti ratio of 20 and fumed silica added at the hydrothermal treatment stage.

3. 4. Effect of Grinding Time

Figure 7 shows the XRD patterns of silica-titania mixtures (Si/Ti = 20) obtained after different grinding times. For all samples, even after a grinding time as short as 3 h, the diffraction peaks assignable to anatase-type titania disappear. However, the UV-visible spectra (Fig. 8) indicate that the samples with short grinding time (3 h and 6 h) still contain octahedral Ti species. After milling for more than 12 h, the absorption band of octahedrally-coordinated Ti species completely disappears, and only an absorption band around 210 nm

Table 1 Si/Ti and Si/Zr Molar Ratios of the Products with Different Grinding Time

Grinding time [h]	Ground silica-titania composite ^{a)}		TS-1 ^{b)}		Washed TS-1 ^{c)}	
	Si/Ti	Si/Zr	Si/Ti	Si/Zr	Si/Ti	Si/Zr
3	22	66	56	172	59	182
6	22	39	56	99	57	93
12	22	20	58	50	59	48
24	23	10	57	23	55	22
48	24	6	66	14	67	14

a) 0.03 mol of fumed silica and 0.006 mol of ST-01 (Si/Ti = 20) ground at 600 rpm in a zirconia pot. b) Fumed silica is added to silica-titania composite to adjust Si/Ti to 50. c) Washed with 0.1 M (1M = 1 mol · dm⁻³) HCl at room temperature.

attributable to tetrahedrally-coordinated Ti species is observed.

However, a longer grinding time seems to have the disadvantage of increased zirconia impurity from the pot and balls. Although no remarkable difference is observed in the XRD patterns of the products with grinding times of 3 to 24 h, after 48 h of milling the intensities of the peaks attributed to zirconia (30.2° and 34.6°) are obviously increased (**Fig. 7 (f)**). The increase in zirconia impurity is directly shown by ICP measurement of the products (**Table 1**); the Si/Zr molar ratio of the ground product increases with increasing grinding time, whereas the Si/Ti molar ratio is practically constant. The Si/Zr ratios of the final TS-1 products are influenced by the molar ratios of these ground mixtures.

Figure 9 shows the XRD patterns of final TS-1 products synthesized from the mechanochemically reacted silica-titania composites obtained above. The crystallinity in terms of peak intensities decreases with increasing grinding time, probably because of the contamination by zirconia. The product synthesized from the mixture without milling shows a double peak around 24.5° (**Fig. 9 (a)**), whereas the other TS-1 materials produced from ground silica-titania composites exhibit a single peak in this region (expanded figure shown as **Fig. 10**). This difference is derived from the symmetrical change of MFI-type topology from monoclinic to orthorhombic, which is usually observed when Ti atoms are incorporated into the silicate framework¹⁾. That is, for TS-1 samples prepared from ground silica-titania composite, Ti atoms are incorporated into the MFI zeolite framework, even though octahedral Ti species remain in some samples.

The synthesized TS-1 materials are used as catalysts for the epoxidation of 1-hexene. **Table 2** exhibits the catalytic performances of these materials. TS-1 material synthesized from silica-titania composite ground for 3 h has low catalytic activity, presumably because the remaining octahedral Ti species (**Fig. 8 (b)**) cannot act as active centers. When the milling time is increased to 6 h or 12 h, the catalytic activity of the TS-1 sample improves with the decrease in octahedral Ti

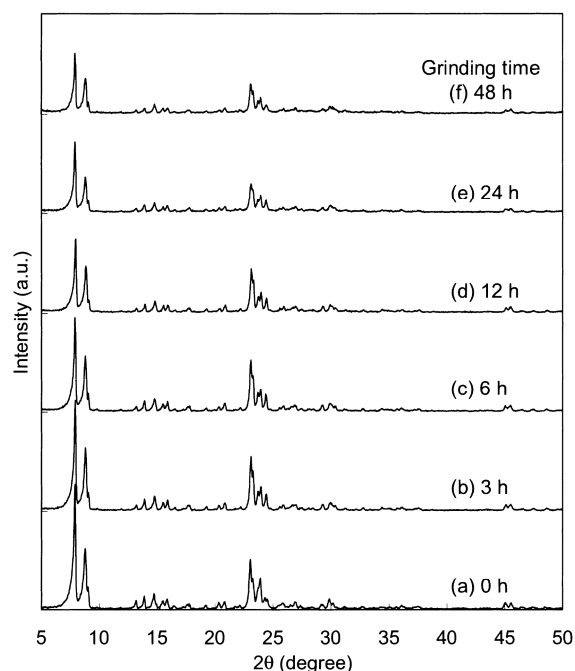


Fig. 9 XRD Patterns of TS-1 Materials Synthesized from Silica-titania Mixtures Ground for (a) 0 h, (b) 3 h, (c) 6 h, (d) 12 h, (e) 24 h, (f) 48 h

species. However, the samples with longer milling times (24 h, 48 h) show considerably lower catalytic activities, although they contain practically only tetrahedral Ti species. As described above, these samples have low crystallinity presumably due to the presence of zirconia impurity (**Fig. 9**). This low crystallinity presumably impairs the surface hydrophobicity of TS-1, resulting in the low catalytic activity^{21)–23)}. Zirconium atoms might also be incorporated into the framework of the MFI structure to reduce the surface hydrophobicity. As a result, TS-1 sample from composite ground for 6 h shows the highest catalytic activity due to the lower Zr content, although octahedral Ti species are still present in this sample.

3.5. Effect of Disk Rotation Speed

Figure 11 shows the UV-visible spectra of silica-titania mixtures ground at 200, 400, 600 and 800 rpm

for 24 h. The product ground at 200 rpm shows an absorption band at 330 nm (Fig. 11 (a)), indicating the preservation of the octahedrally-coordinated Ti species. The XRD pattern (Fig. 12 (a)) contains a small peak at around 25.2° corresponding to the presence of anatase titania. Grinding at 200 rpm would not produce enough impact energy to obtain completely amorphous material. In contrast, the mixtures ground at more than 400 rpm show the absorption band mainly attributable to the tetrahedrally-coordinated Ti species (Fig. 11 (b)-(d)) and no diffraction peaks assignable to anatase titania (Fig. 12 (b)-(d)). However, the excessively fast disk rotation speed results in increased zirconia impurities, as the sample ground at 800 rpm shows clear diffraction peaks attributable to zirconia (Fig. 12 (d)). The optimal disk rotation speed seems to be 400-600 rpm, considering the complete absence of octahedral Ti species and the amount of impurity.

Figure 13 shows the XRD patterns of the final TS-1 products. The TS-1 samples prepared from the mixture milled at 200 rpm show a double peak 24.5° , implying that the Ti atoms are not effectively incorporated into the zeolite framework because of insufficient milling.

Table 3 shows the catalytic performances of the TS-1 materials in the epoxidation of 1-hexene. TS-1

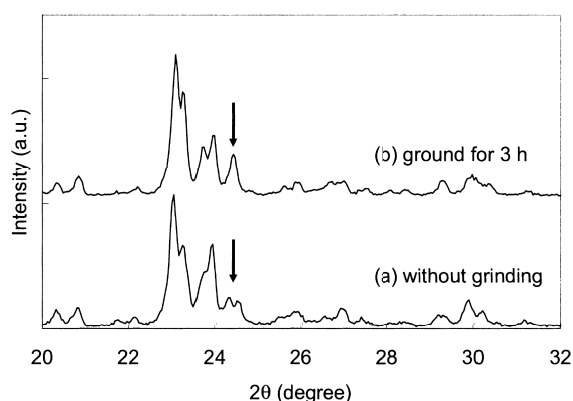


Fig. 10 XRD Patterns of TS-1 Materials Synthesized from Silica-titania Mixtures (a) without Grinding and (b) Ground for 3 h

material synthesized from silica-titania composite ground at 200 rpm has low catalytic activity because of the lower content of tetrahedrally-coordinated Ti sites due to insufficient milling. In contrast, the TS-1 material prepared from the composite ground at 400 rpm, which contains practically only tetrahedrally-coordinated Ti species, show higher catalytic activity. However, too fast disk rotation speed in this case causes large contamination by zirconia impurity to spoil the catalytic activity of TS-1. As a result, higher disk rotation speed during mechanochemical reaction could reduce the catalytic activity of the TS-1 material.

4. Conclusion

Study of various milling parameters on the properties of silica-titania mixtures and final TS-1 materials shows the following. Using small starting material particles and dense milling media mixes the titania and silica effectively. Longer grinding time as well as faster disk rotation speed greatly promotes the mechanochemical reaction between titania and silica. However, too long

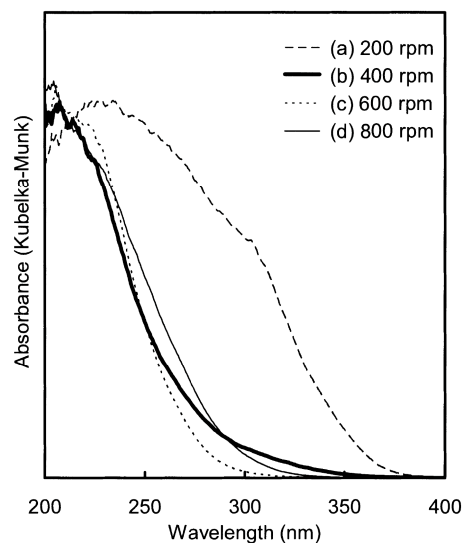


Fig. 11 UV-visible Spectra of Silica-titania Mixtures Ground at (a) 200 rpm, (b) 400 rpm, (c) 600 rpm, and (d) 800 rpm

Table 2 Effect of Grinding Time on the Catalytic Performance of Resulting TS-1 Material

Grinding time [h]	Si/Ti	Si/Zr	Conversion ^(a) [mol%]	TON ^(b)	Selectivity [mol%]		H ₂ O ₂ efficiency ^(c) [mol%]
					epoxide	diol	
3	59	182	7.4	17	92.5	7.5	92
6	57	93	15.0	33	94.3	5.7	94
12	59	48	11.2	26	92.0	8.0	84
24	55	22	1.6	4	>99.9	trace	92
48	67	14	1.4	4	>99.9	trace	100

Catalyst 0.05 g, 1-hexene 10 mmol, H₂O₂ 3 mmol, acetone 5 ml, 60°C, 3 h.

a) Oxidant-based conversion. b) Turnover number (mol-(epoxide + diol)/mol-Ti). c) 100 - decomposed H₂O₂ (mol%).

Table 3 Effect of Disk Rotation Speed on the Catalytic Performances of Resulting TS-1 Materials

Disk rotation speed [h]	Si/Ti	Si/Zr	Conversion ^{a)} [mol%]	TON ^{b)}	Selectivity [mol%]		H ₂ O ₂ efficiency ^{c)} [mol%]
					epoxide	diol	
200	68	>1600	3.9	10	>99.9	trace	85
400	55	94	12.6	27	94.2	5.8	82
600	55	22	1.6	4	100	0	92
800	78	10	0.4	2	100	0	95

Catalyst 0.05 g, 1-hexene 10 mmol, H₂O₂ 3 mmol, acetone 5 ml, 60° C, 3 h.

a) Oxidant-based conversion. b) Turnover number (mol-(epoxide + diol)/mol-Ti). c) 100 – decomposed H₂O₂ (mol%).

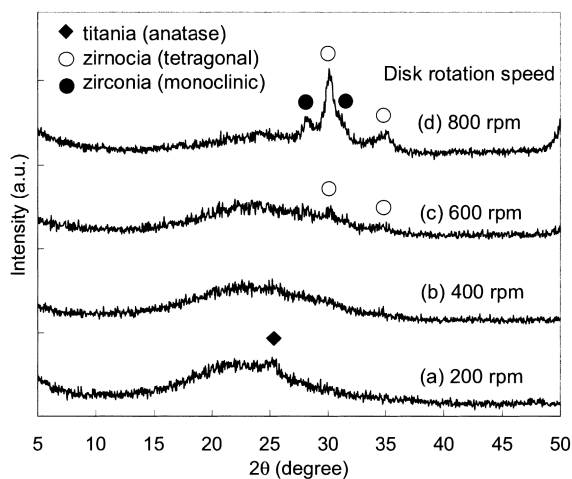


Fig. 12 XRD Patterns of Silica-titania Mixtures Ground at (a) 200 rpm, (b) 400 rpm, (c) 600 rpm, and (d) 800 rpm

grinding time or excessively fast disk rotation speed increases the amount of impurity zirconia derived from the milling pot and balls, which hinders the nucleation of the MFI phase and reduces the catalytic activity of the TS-1 material.

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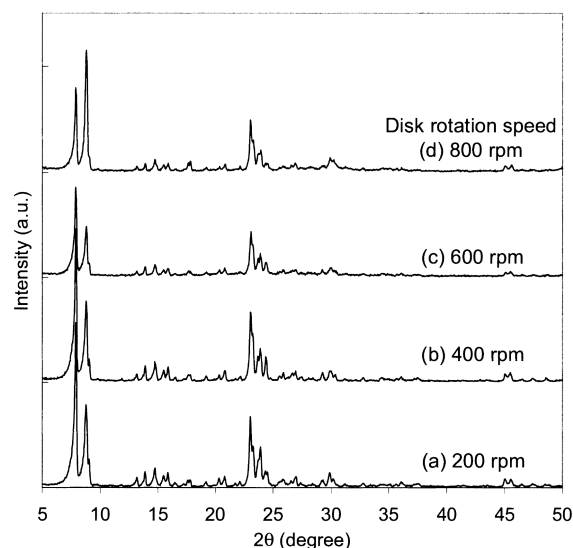


Fig. 13 XRD Patterns of TS-1 Materials Synthesized from Silica-titania Mixtures Ground at (a) 200 rpm, (b) 400 rpm, (c) 600 rpm, and (d) 800 rpm

要 旨

メカノケミカル法によるチタノシリケートの合成

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新しく開発したメカノケミカル法により MFI 型チタノシリケート TS-1 を合成し、メカノケミカル反応の条件と生成物の物性について調べた。メカノケミカル法は、チタニアおよびシリカ粉末を遊星ボールミルにより粉砕して得られるシリカ-チタニア複合粉末を前駆体として用い、構造指向剤存在下で水熱処理することによりチタノシリケートを得る手法である。得られた生成物について、X 線回折、紫外-可視吸収など

によりキャラクターゼーションを行い、アルケン酸化反応に対する触媒活性を調べた。メカノケミカル反応条件、つまりボールミルの回転速度、粉砕時間、原料比など前駆体合成時の反応条件は最終生成物の物理的、化学的性質に大きな影響を及ぼし、高い触媒活性を示す TS-1 を得るための最適値が存在することが分かった。

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