Properties of Ti-Beta Zeolites Synthesized by Dry-Gel Conversion and Hydrothermal Methods

Takashi Tatsumi* and Nizamidin Jappar

Engineering Research Institute, School of Engineering, The University of Tokyo, Yayoi, Tokyo 113-8656, Japan

Received: March 25, 1998; In Final Form: June 10, 1998

The large-pore beta zeolite containing Ti has been synthesized in the presence of alkali cations (Na^+) by a dry-gel conversion (DGC) technique using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent. The obtained Ti-beta zeolites were compared with hydrothermally synthesized (HTS) Ti-beta. It was found that Ti-beta-DGC samples adsorbed less water (12–13 wt %) than Ti-beta-HTS (19 wt %), indicating that Ti-beta-DGC is more hydrophobic than Ti-beta-HTS. We propose that this leads to a higher activity for the former in the oxidation of cyclohexane. Upon being washed with H_2SO_4, the turnover number (TON) of DGC samples slightly increased for the oxidation of cyclohexane. DGC and HTS samples demonstrated no significant difference in the activity for oxidation reactions of unsaturated alcohols and C_6–C_8 cyclic alcohols.

1. Introduction

Titanium silicalites (TS-1 and TS-2) are highly efficient for the selective oxidation of a large number of organic substrates, such as alkenes, alcohols, aromatics, and alkanes, using H_2O_2 as the oxidant under mild reaction conditions.[1] Unlike the group IV–VI metal oxide catalysts, titanium silicalites are active in the presence of diluted aqueous solutions of hydrogen peroxide, whereas organic hydroperoxides, such as *tert*-butyl hydroperoxide (TBHP), are the oxidants of choice for the former catalysts.[2] The differences can be partially ascribed to the hydrophobic character of titanium silicalites, which favors the adsorption of the organic substrates over the more polar water molecules present in the H_2O_2 solution, thus maintaining the Ti sites inside the zeolite pores in the organic-rich environment. The activity for the oxidation of 1-hexene and *n*-octane on TS-1 is not modified by the use of either aqueous or anhydrous solutions of H_2O_2, but activity of amorphous TiO_2–SiO_2 catalysts is strongly inhibited when the aqueous H_2O_2 solution is used as oxidant.[3]

Recently, a large-pore Ti-containing zeolite, Ti-beta, has been hydrothermally synthesized from gels containing tetraethylammonium hydroxide (TEAOH) as a structure directing agent and some aluminum as a framework constituent.[4] Ti-beta proved to be an active catalyst for the oxidation of alkanes and alkenes, either by using H_2O_2 or TBHP as oxidants.[5–7] Due to its large pore size, Ti-beta was shown to be more active than TS-1 for the oxidation of bulky substrates such as cyclic and branched molecules.[5,6] However, an additional factor, viz., the presence of aluminum in the framework of Ti-beta, can contribute to the different catalytic behavior observed between Ti-beta and TS-1;[7] the framework Al introduces additional acidity into Ti-beta, which is reflected in the lower selectivity to the epoxide during olefin epoxidation than on TS-1, since residual protons associated to Al catalyze the opening of the oxirane ring with the corresponding formation of glycols and glycol derivatives.[6,7] Furthermore, aluminum atoms incorporated into the framework lead to a detrimental effect on the activity for epoxidation.[8] On the other hand, thus prepared Ti-beta has a high density of connectivity defects. Hence the presence of Al and large concentration of internal and external silanol groups confers a rather hydrophilic character on Ti-beta in contrast to the organophilic characteristics of TS-1.

The beta structure is thought to be an unstable kinetic phase which crystallizes merely under very specific conditions. Unlike the molecular sieve having an MFI structure which may crystallize using a wide variety of templates, Ti-beta with SiO_2/Al_2O_3 higher than 200 could not be obtained by the conventional hydrothermal synthesis method.[4,7] Even in the case of synthesis with a lower SiO_2/Al_2O_3 ratio, the product yield was often very low.[7] There is therefore a strong incentive for the preparation of Ti-beta with a better zeolite yield by using new templates and methods.

Improved synthesis methods (e.g., Cogel method,[9] seeding techniques,[10] fluoride method,[11] and gas–solid[12] and liquid–solid[13] isomorphous substitution have been developed to obtain the Ti-beta zeolites with high yields. The first successful preparation of Ti-beta without the need for Al and alkali cations in the gel was patented by ARCO using a benzyl-substituted diquaternary ammonium cation as a novel structure-directing agent.[14] Aluminum-free Ti-beta was synthesized using di-(cyclohexylmethyl)dimethylammonium as the structure-directing agent[15] and was used for Meerwein–Ponndorf–Verley–Oppenauer reactions[16,17] and epoxidation reactions.[18] In the crystallization of a variety of zeolites, the vapor-phase transport (VPT) method is also an efficient one,[19–21] which involves crystallization of a dry gel in the presence of volatile structure-directing agents and steam. However, in many cases, the VPT method is not applicable since most of the zeolite preparations need nonvolatile structure-directing agents. Recently, Rao and Matsukata[22,23] developed a new effective technique named dry-gel conversion (DGC) for the synthesis of beta zeolite with a high SiO_2/Al_2O_3 molar ratio up to 900 using TEAOH as the template. More recently, we have succeeded in synthesizing Ti-beta zeolites in the presence of certain amount of sodium by the DGC method using TEAOH.[24] The product yield was more than 95%. In the oxidation reaction of cyclohexene, the Ti-beta exhibited complete conversion and 100% of selectivity of H_2O_2 to the oxidized products.

---

* To whom correspondence should be addressed.

Properties of Ti-Beta Zeolites

J. Phys. Chem. B, Vol. 102, No. 37, 1998 **7127**

TABLE 1: Synthesis of Ti-Beta Materials

	in gel (mol %)			in zeolite (mol %)				H_2SO_4 washed (mol %)		
sample	Ti/ $(T^{IV} + Al)$	Na/ $(T^{IV} + Al)$	Al/ $(T^{IV} + Al)$	Ti/ $(T^{IV} + Al)$	Na/ $(T^{IV} + Al)$	Al/ $(T^{IV} + Al)$	crystallinity (%)	Ti/ $(T^{IV} + Al)$	Na/ $(T^{IV} + Al)$	Al/ $(T^{IV} + Al)$
DGC-1	3.19	0.98	0.16	3.30	0.52	0.12	70	2.32	0.23	0.12
DGC-2	3.20	0.68	0.29	3.12	0.64	0.30	81	2.17	0.23	0.12
DGC-3	3.18	0.99	0.29	3.12	0.92	0.28	74	2.29	0.22	0.15
DGC-4	3.18	0.98	0.29	3.12	1.02	0.27	82	2.66	0.18	0.15
DGC-5	3.17	0.98	0.80	3.25	1.04	0.62	85	3.11	0.10	0.49
DGC-6	3.20	0.99	0.16	3.30	0.57	0.12	80			
DGC-7	3.18	0.98	0.16	3.30	0.66	0.12	80			
DGC-8	3.20	1.93	0.29	3.39	1.95	0.30	38			
DGC-9	3.18	0.98	0.13		nd[a]		0			
DGC-10	3.18	0.39	0.29		nd		0			
HTS-1	2.43		0.24	3.43		0.42	85	1.92		0.23
HTS-2	2.43		0.24	2.17		0.65	85	1.42		0.45
TS-1	3.0			1.25			100			

[a] nd = no data.

The aim of this work is to further investigate the properties of the Ti-beta zeolite synthesized by the dry-gel conversion method (Ti-beta-DGC) in comparison with the Ti-beta synthesized by the hydrothermal method (Ti-beta-HTS).

2. Experimental Section

Synthesis and Characterization of Ti-beta Catalyst. Typically, Ti-beta was synthesized according to the following procedure: 0.58 g of tetrabutyl orthotitanate (97 wt %, Kanto) was first added to 4.0 g of distilled water, and to the resulting suspension was added 2.0 g of H_2O_2 (31 wt %, MGC) after 1 h. The mixture was stirred at room temperature for 1 h, leading to solution A containing peroxide titanate. Solution B was prepared by dissolving 0.0124 g of anhydrous $NaAlO_2$ (Koso) and 0.015 g of NaOH (96 wt %, Koso) in 8.0 g of TEAOH (40 wt % in water, Alfa) at room temperature with stirring for 1 h. Solution B was added to solution A, and stirring was continued for 1.5 h. Then, 3.0 g of fumed silica (Aerosil-200, Nippon Aerosil) was added under vigorous stirring. A clear homogeneous solution obtained after 2 h was heated to 353 K and dried while stirring. When the gel became dry, it was ground into fine powder (chemical composition: SiO_2:TiO_2:Al_2O_3:Na_2O: TEAOH = 304:10:0.46:1.55:132.5) and transferred into a special autoclave, where water as source of steam was poured into the bottom. The crystallization was carried out in steam first at 403 K for 96 h, subsequently at 448 K for 18 h under autogenous pressure. The obtained Ti-beta zeolite product (Ti-beta-DGC) was washed with distilled water, dried at 308 K for 10 h, and calcined at 793 K for 10 h in the flow of air. The hydrothermally synthesized Ti-beta (Ti-beta-HTS) was obtained according to the recipe described in the literature.[7] The Ti-beta zeolites were treated with 1 M H_2SO_4 at room temperature for 12 h and then washed with distilled water, dried at 308 K for 10 h, and calcined at 793 K for 5 h in the flow of air.

X-ray powder diffraction patterns were collected on a Rigaku Denki RU-200A diffractometer using Cu Kα radiation. SEM micrographs were obtained with a JEOL JSM 5400 microscope equipped with an ED probe. The Fourier transformed infrared spectra (FTIR) were recorded in the transmittance mode on a Perkin-Elmer 1600 spectrometer using conventional heatable IR cells connected to vacuum-gas manipulation apparata. UV−vis spectra were obtained on a Hitachi 340 spectrophotometer. Thermogravimetry (TG) was performed on an ULVAC TGD-7000 differential thermogravimetric analyzer.

Catalytic Reactions. The alkane oxidation reactions were conducted at 373 K for 5 h in an autoclave (30 mL). In a typical

experiment, 18.7 mmol of alkane, 10 mL of solvent, 0.1 g catalyst, and 9.3 mmol of hydrogen peroxide (31% aq solution) were mixed in a Teflon inner placed in the autoclave and heated to the desired temperature under vigorous agitation. The unsaturated alcohol oxidation reactions were carried out at 323 K for 3 h in a glass round-bottom flask (50 mL) fitted with a condenser and a magnetic stirrer. A mixture of 16.5 mmol of unsaturated alcohol, 10 mL of solvent, 0.1 g catalyst, and 5 mmol of hydrogen peroxide (31% aq solution) was heated in the flask to the desired temperature under vigorous agitation. The oxidation of cyclic alcohols was carried out at 338 K. After the reaction was completed, the catalysts were separated by filtration and the products were analyzed on a Shimadzu GC 14A gas chromatograph equipped with a 50 m OV-1 capillary column. Cycloheptanone or 2-pentanone was used as an internal standard.

3. Results and Discussion

Characterization. The yield of Ti-beta zeolite is higher than 95 wt % based on silica for the DGC method in contrast to the low (∼15 wt %) yield for the HTS method. The Ti-beta-DGC synthesized from colloidal silica with a high content of sodium (Na_2O/SiO_2 = 0.04) is well crystallized and the compound was used as a reference of the crystallinity.

The composition of the gel in the synthesis of Ti-beta-DGC significantly affects the crystallinity and oxidation activity of the final products. The composition and crystallinity of Ti-beta-DGC and Ti-beta-HTS are shown in Table 1. The presence of Na is unfavorable for the synthesis of Ti-beta by the hydrothermal method.[7] However, in the case of the DGC method, the presence of a certain amount of Na species in the gel is necessary. At Na contents lower than 0.4 mol %, the products are amorphous. With a high content of Na, the products exhibit low crystallinity (see, e.g., DGC-8 in Table 1). The amount of Al in the gel also influences the crystallinity of the products. At Al contents Al/(Si+Ti+Al) lower than 0.16 mol %, only amorphous products were obtained. Upon treatment of sample with 1 M H_2SO_4 at room temperature, the Al and Na contents of Ti-beta-DGC are remarkably decreased and Ti is also slightly lost.

The UV−vis spectra of the calcined Ti-beta synthesized by the DGC and HTS methods are presented in Figure 1. All the samples exhibit a band at 205−230 nm, resulting from the charge transfer from oxygen atoms to Ti^{4+}, characteristic of tetrahedrally coordinated Ti in the framework and is generally observed for Ti-substituted molecular sieves.[25] The absence of
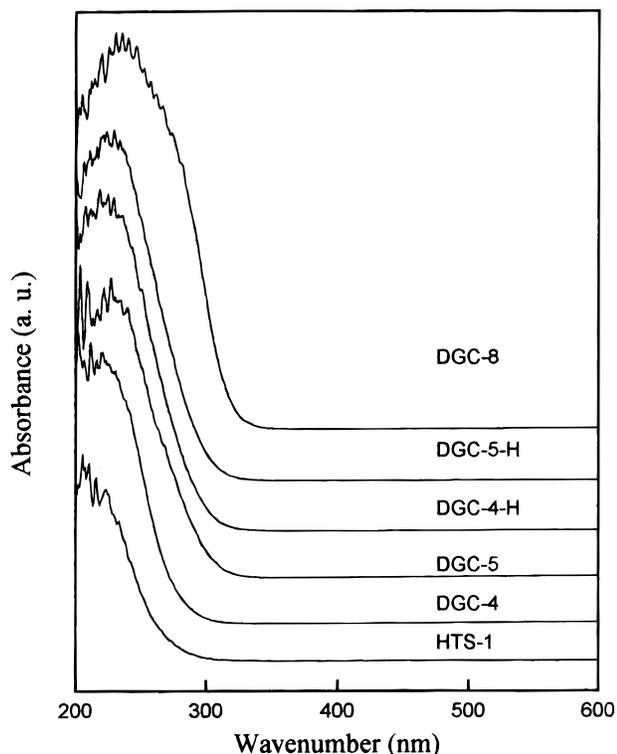
Figure 1. UV−vis spectra of Ti-beta zeolites. DGC: dry-gel conversion methods sample, HTS: hydrothermally synthesized sample. H: H_2SO_4-washed sample.

the band between 310 and 350 nm indicates that anatase-like phase is not formed in these samples during crystallization. DGC-8, synthesized in the presence of large amount of alkali cations, shows a shoulder at 270 nm, which can be attributed to hexacoordinated Ti species belonging to an amorphous titanosilicate phase.[25] The HTS sample synthesized hydrothermally in the absence of sodium shows a band at about 205 nm and Ti-beta-DGC synthesized in the presence of sodium exhibits band at 205−230 nm. It has been reported that the presence of alkali cation could prevent titanium from incorporating into

the framework during hydrothermal syntheses.[5] By the DGC method, however, the existence of Na below 1 mol % does not affect the incorporation of titanium into the framework.

Figure 2 shows the SEM images of Ti-beta zeolite synthesized by the DGC and HTS methods. The particle size of the products for both the DGC and HTS samples is rather uniform and no amorphous phase can be found in the samples. The average crystal size of the Ti-beta-DGC (20−40 nm) is much smaller than that of the Ti-beta-HTS (150−400 nm). The formation of such small uniform crystals from the dry gel powder is of particular interest to understand the mechanism of zeolite formation, possibly indicating a large number of nuclei are formed during the crystallization of Ti-beta-DGC.

The IR spectra of the hydroxyl groups of the Ti-beta zeolites recorded as a function of the outgassing temperature are illustrated in Figure 3. For the DGC sample (Ti-beta-DGC-5 H_2SO_4-washed), an intense band at 3740 cm^{-1} is observed together with broad shoulder bands ranging from 3610 cm^{-1} to 3300 cm^{-1}. For the HTS sample, three types of OH bands can be distinguished: a strong band at 3740 cm^{-1}, a weak band at 3606 cm^{-1}, and shoulder bands ranging from 3600 to 3300 cm^{-1}. With increasing outgassing temperature, the band at 3740 cm^{-1} is sharpened and the broad shoulder bands are substantially decreased in intensity.

The band at 3740 cm^{-1} is ascribed to the isolated silanol groups, the band at 3606 cm^{-1} to the Si−O−Al groups, and the broad band (3610−3300 cm^{-1}) to the H-bonded OH groups of silanol groups.[26−28] The broad feature of the latter band should be due to the interaction between the hydroxyl groups at internal defects which results in the formation of hydrogen bonded chains. The length and configuration of such chains vary depending upon the structure of the defects of the zeolites.[28] Heating at the elevated temperature in vacuo leads to a decrease in the length of the chain and to an increase in the number of the isolated silanol species due to the removal of water in the zeolites and, consequently to the decrease in intensity of the broad band around 3500 cm^{-1}. Ti-beta-DGC-5 (H_2SO_4 washed) sample contains a negligible amount of Na (Na_2O/SiO_2 = 0.0005, Na_2O/Al_2O_3 = 0.2), which cannot influence IR spectra
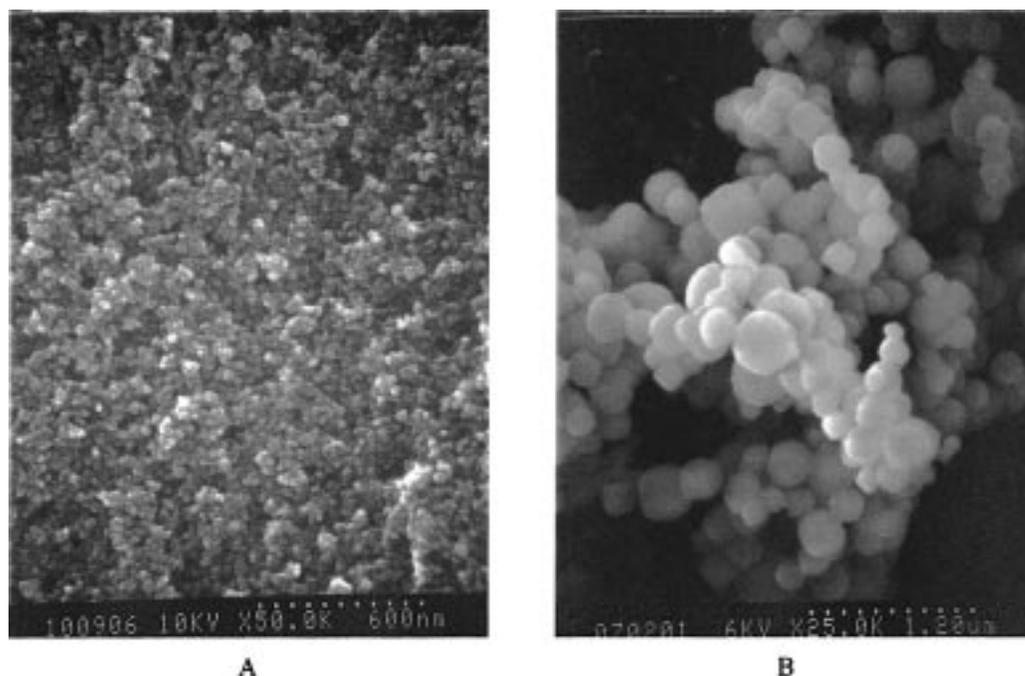
Figure 2. SEM of Ti-beta synthesized by (A) DGC method and (B) HTS method.

Properties of Ti-Beta Zeolites

J. Phys. Chem. B, Vol. 102, No. 37, 1998 **7129**
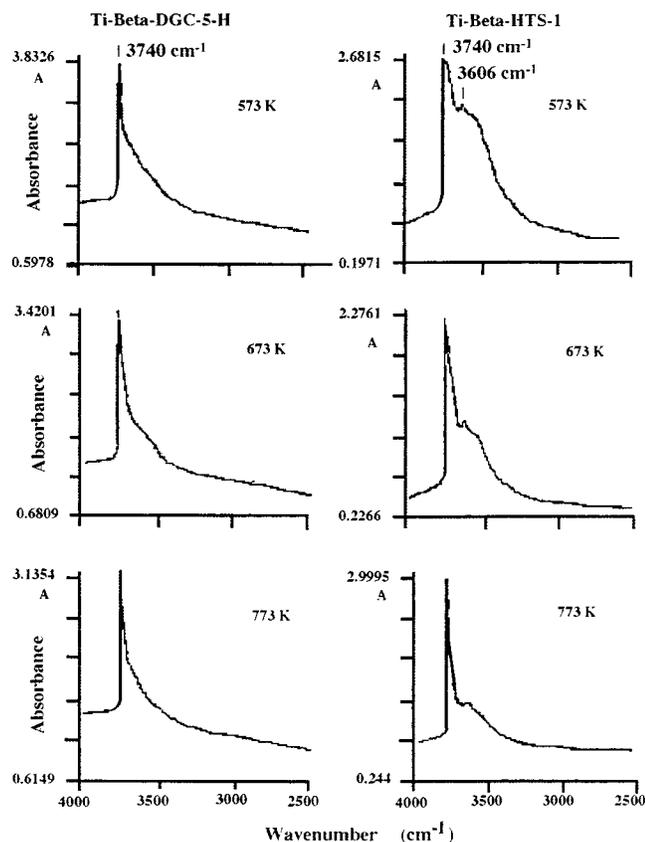
Figure 3. FT-IR spectra of Ti-beta. H: H_2SO_4-washed sample.

Figure 4. Desorption of water on Ti-beta. DGC: dry-gel conversion methods sample. HTS: hydrothermally synthesized sample. H: H_2SO_4-washed sample.

in the O−H region. Compared with the Ti-beta-HTS sample, the intensity of the broad band for the Ti-beta-DGC sample is much weaker, which suggests that the Ti-beta-DGC contains less defects than the Ti-beta-HTS.

The amount of water absorbed on the calcined Ti-beta samples which were contacted with moisture over saturated aqueous NH_4Cl solution for 24 h is determined thermogravimetrically (Figure 4). The weight losses of Ti-beta-DGC samples are about 12−13%. The weight losses are independent of the contents of Na or Al. The amount of water desorbed from Ti-beta-HTS-1 (19 wt %) is larger than that from DGC samples, implying that Ti-beta-DGC is more hydrophobic than Ti-beta-HTS, in agreement with the lower density of the defects on the former.

Influence of Ti-beta Properties on its Catalytic Activity in the Oxidation of Cyclohexane. Table 2 shows the catalytic

activities of Ti-beta samples synthesized by the DGC and HTS methods in the oxidation of cyclohexane with H_2O_2 at 373 K. Cyclohexanol and cyclohexanone are formed from cyclohexane over the Ti-beta samples. The Ti-beta-DGC samples exhibit higher turnover number (TON) and H_2O_2 selectivity than Ti-beta-HTS samples. The difference is probably related to the hydrophobic character of Ti-beta zeolites. For hydrophilic Ti-beta zeolites, the Ti active sites are covered by water molecules, and therefore, cyclohexane molecules are made to be not easily accessible to the active sites, as will be discussed below.

Upon treatment of the Ti-beta-DGC samples (Table 1) with 1 M H_2SO_4 at room temperature, large amounts of Al and Na are eliminated and Ti is also slightly lost. As a result, the turnover number (TON) of the samples is significantly increased. This is in agreement with the previous findings; the catalytic activities for the hydrothermally synthesized Ti-containing zeolites are decreased with increasing Al for Ti-beta[5] and Na content for TS-1.[2,8,30] The cyclohexane oxidation activity of H_2SO_4-washed Ti-beta-HTS sample is, however, low compared

TABLE 2: Activity of Ti-Beta Catalysts in the Oxidation of Cyclohexane with $H_2O_2^a$

| | calcined | | | | | | | H_2SO_4 washed | | | | | | |
| | cyclohexane | | selectivity^c (%) | | | H_2O_2 (%) | | cyclohexane | | selectivity^c (%) | | | H_2O_2 (%) | |
sample	conversion (%)	TON^b	OL	ONE	EHK	conversion	selectivity	conversion (%)	TON^b	OL	ONE	EHK	conversion	selectivity
DGC-1	11.1	46	79	21		93	29	23	67	83	12	4.6	91	25
DGC-2	11.5	47	81	19		89	31	20	62	82	12	5.9	90	27
DGC-3	11.3	48	78	22		92	30	23	69	80	13	7.1	91	31
DGC-4	10.1	42	84	16		90	26	17	45	80	12	8.2	92	23
DGC-5	9.8	41	83	17		89	26							
DGC-6	12.1	51	74	26		90	34							
DGC-7	11.2	47	77	23		91	30							
HTS-1	6.4	26	81	3.5	16	90	16	2.2	8.8	55	43	3	79	4.0
HTS-2	5.3	30	84	7.1	0.6	90	12	2.0	9.1	76	13	11	78	3.0
TS-1	0.4	5.4	48	52		88	1.3							

^{a} Reaction conditions: reaction temperature = 373 K, reaction time = 5 h, 18.7 mmol of cyclohexane, 9.3 mmol of H_2O_2 (31 wt % in water), 10 mL of methanol (solvent), 0.1 g of catalyst. ^{b} Moles of products/moles of Ti in the catalyst. ^{c} ONE, cyclohexanone; OL, cyclohexanol; EHK, cyclohexyl methyl ether, hemiketal, and ketal.

TABLE 3: Oxidation of Cyclic Alcohols with H₂O₂ over Ti-Beta[a]

cyclic alcohol	catalyst	conversion (%)	turnover number (mol/mol-Ti)	H_2O_2 (%) conversion	selectivity
cyclohexanol	DGC	13.3	39	80	55
	HTS	13.0	37	78	55
cyclooctanol	DGC	14.6	43	80	61
	HTS	14.9	42	75	65

[a] Reaction conditions: Reaction temperature = 338 K, reaction time = 3 h, 16.5 mmol of cyclic alcohol, 5 mmol of H_2O_2 (31 wt % in water), 10 mL of acetonitrile (solvent), 0.1 g of catalyst (DGC, Ti-Beta-DGC-7; HTS, Ti-beta-HTS-1).

TABLE 4: Oxidation of Unsaturated Alcohols with H₂O₂ on Ti-Beta[a]

unsaturated alcohol	catalyst	conversion (%)	TON (mol/mol-Ti)	selectivity (%) aldehyde	epoxy-1-aldehyde	epoxy-1-ol	H_2O_2 (%) conversion	selectivity
4-penten-1-ol								
	DGC	10.9	34	2.9	1.3	96	60	60
	HTS	10.0	29	5.4	2.1	93	58	57
3-methyl-2-buten-1-ol								
	DGC	11.2	35	23	17	60	77	56
	HTS	9.9	30	26	25	49	77	52

[a] Reaction conditions: reaction temperature 323 K, reaction time = 3 h, 16.5 mmol of unsaturated alcohol, 5 mmol of H_2O_2 (31 wt % in water), 10 mL of solvent (acetonitrile), 0.1 g of catalyst (DGC, Ti-beta-DGC-5; HTS, Ti-beta-HTS-1).

to that of the unwashed sample, mainly due to the large decrease in the amount of Ti. The activity of TS-1 for this reaction is negligible, probably because of cyclohexane is too large to easily diffuse into the channel of TS-1. When Ti-beta-HTS and H₂-SO₄-washed Ti-beta-DGC samples are used as catalysts, the following acid-catalyzed secondary reactions take place between the cyclohexanol and cyclohexanone with the solvent MeOH. In the first case, cyclohexyl methyl ether is formed (a), while reaction b leads first to the formation of hemiketal followed by formation of ketal through its reaction with MeOH. In the reaction conditions, the reactions b are predominant. The extent of these secondary reactions is small when the unwashed Ti-beta-DGC is used as the catalyst, because of the resulting reduced acidity.
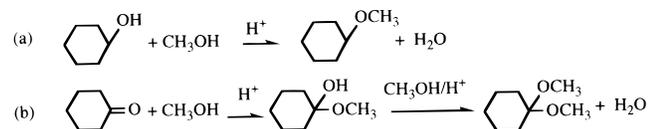
Oxidation of Cyclic Alcohols on Ti-Beta. We have studied the oxidation of cyclic alcohols on the Ti-beta catalysts using hydrogen peroxide as oxidant. The experiments are performed at 338 K in acetonitrile solvent. Under these reaction conditions, only the corresponding ketones are formed from cyclic alcohols. As shown in Table 3, reactivity of cyclooctanol is slightly higher than that of cyclohexanol. The differences in the conversion between cyclohexanol and cyclooctanol are similar for the Ti-beta-DGC and Ti-beta-HTS samples, although the latter has much larger average crystal size than the former. This indicates that the conversion is not influenced by diffusional factors due to the large pore sizes of beta zeolites.

Furthermore, the fact that larger cyclooctanol exhibits higher reactivity than cyclohexanol suggests that the reactivity of cyclooctanol is intrinsically higher than that of cyclohexanol. The Ti-beta-DGC and Ti-beta-HTS samples show similar activity for oxidation of both alcohols. In contrast, the relatively hydrophobic Ti-beta-DGC samples exhibit higher activity for the oxidation of alkanes than Ti-beta-HTS, as described above. These phenomena may be due to the hydrophobicity/hydrophilicity of the substrate. The concentration of the reactants in

the relatively hydrophilic Ti-beta channels decreases with hydrophobicity of the reactants because of the preferential adsorption of water, resulting in the decreases in the rate of oxidation. For relatively hydrophobic zeolites, the hydrophobic reactants can be competitively adsorbed into the zeolite channels. However, hydrophilic reactants would have no difficulty in adsorbing into the zeolite channels in the presence of water molecules, regardless of hydrophobicity/hydrophilicity of the zeolite surface.

Another explanation for the higher activity of the Ti-beta-DGC samples for the cyclohexane oxidation compared to the Ti-beta-HTS ones may be the small crystal sizes of the former. However, there is no virtual difference in the activity for oxidation of alcohols, hydrophilic substrates, between the two samples prepared by the different methods, indicating the higher activity of the Ti-beta-DGC samples for the cyclohexane oxidation is not due to the smaller crystal size but to the higher hydrophobicity.

Oxidation of Unsaturated Alcohols on Ti-Beta. The effects of the structure of C_5 unsaturated alcohols on the reactivity toward oxidation are investigated; pertinent data are shown in Table 4. The experiments are conducted at 323 K in acetonitrile used as solvent. Similar reactivity is observed between 3-methyl-2-buten-1-ol and 4-penten-1-ol. The presence of the electron-donating methyl group increased not only electric density of the C=C double bond of 3-methyl-2-buten-1-ol but also steric restriction to access to the active site in the Ti-beta, resulting in the decrease in the selectivity for the epoxidation. The epoxide/aldehyde ratios in the oxidation of 3-methyl-2-buten-1-ol over TS-1[31] and Ti-beta are 0.23 and 1.4, respectively. These results are accounted for by assuming that the steric restriction in the large pore beta zeolite are less than that in TS-1.

The Ti-beta-DGC catalyst shows slightly higher activity and higher selectivity for epoxidation than the Ti-beta-HTS catalyst. This might be also related to the higher hydrophobic character of the Ti-beta-DGC sample than the Ti-beta-HTS sample; more hydrophobic Ti-beta favors epoxidation against alcohol oxidation and vice versa. Thus it is possible that the hydrophobicity/hydrophilicity affect the chemoselectivity as well as the activity for the liquid-phase oxidation.

Properties of Ti-Beta Zeolites

J. Phys. Chem. B, Vol. 102, No. 37, 1998 **7131**

4. Conclusions

From the present study, the following conclusions can be drawn: (1) The large-pore beta zeolite containing Ti can be synthesized in the presence of alkali cations (Na$^+$) by the dry-gel conversion (DGC) technique using TEAOH as the structure-directing agent. The presence of Na less than 1.0 mol % does not affect the incorporation of titanium into the framework of beta zeolites.

(2) Ti-beta-DGC adsorbs less amount of water than Ti-beta-HTS, indicating the higher hydrophobicity of the former zeolite. The intensity of the broad infrared band ranging from 3610 to 3300 cm^{-1}, associated with hydrogen-bonded hydroxyl groups resulting from the defects in the zeolite structure, is lower for Ti-beta-DGC than for Ti-beta-HTS.

(3) In the oxidation of hydrophobic substrate, such as cyclohexane, the Ti-beta-DGC samples show higher activity than Ti-beta-HTS, whereas they show similar activity in the oxidation of alcohols. This is interpreted in tems of high hydrophobicity of Ti-beta-DGC compared to that of Ti-beta-HTS.

References and Notes

(1) Notari, B. *Adv. Catal.* **1996**, *41*, 253.
(2) Sheldon, R. A. *J. Mol. Catal.* **1980**, *7*, 107.
(3) Khouw, C. B.; Dartt, C. B.; Davis, M. E. *J. Catal.* **1994**, *149*, 195.
(4) Camblor, M. A.; Corma, A.; Martinez, A.; Perez-Pariente, J. *J. Chem. Soc., Chem. Commun.* **1992**, 589.
(5) Corma, A.; Camblor, M. A.; Esteve, P.; Martinez, A.; Perez-Pariente, J. *J. Catal.* **1994**, *145*, 151.
(6) Corma, A.; Esteve, P.; Martinez, A.; Valencia, S. *J. Catal.* **1995**, *152*, 18.
(7) Camblor, M. A.; Corma, A.; Perez-Pariente, J. *Zeolites* **1993**, *13*, 82.
(8) Camblor, M. A.; Corma, A.; Martinez, A.; Perez-Pariente, J.; Primo, J. *Stud. Surf. Sci. Catal.* **1993**, *78*, 393.
(9) Camblor, M. A.; Costantini, M.; Corma, A.; Gilbert, L.; Esteve, P.; Martinez, A.; Valencia, S. *Appl. Catal.* **1995**, *133*, L185.
(10) Camblor, M. A.; Costantini, M.; Corma, A.; Gilbert, L.; Esteve, P.; Martinez, A.; Valencia, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1339.
(11) Camblor, M. A.; Corma, A.; Valencia, S. *Chem. Commun.* **1996**, 2365.
(12) Rigutto, M. S.; De Ruiter, R.; Niederer, J. P. M.; Van Bekkum, H. *Stud. Surf. Sci. Catal.* **1994**, *84*, 2245.
(13) Reddy, J. S.; Sayari, A. *J. Chem. Soc., Chem. Commun.* **1995**, 23.
(14) Saxton, R. J.; Crocco, G. L.; Zajacek, J. G.; Wijesekea, K. S. Eur. Patent 1994, 659 685 A1.
(15) van del Waal, J. C.; Lin, P.; Rigutto, M. S.; van Bekkum, H. *Stud. Surf. Sci. Catal.* **1997**, *105*, 1093.
(16) van del Waal, J. C.; Tan, K.; van Bekkum, H. *Catal. Lett.* **1996**, *41*, 63.
(17) van del Waal, J. C.; Kunkeler, P. J.; Tan, K.; van Bekkum, H. *J. Catal.* **1998**, *173*, 74.
(18) van del Waal, J. C.; van Bekkum, H. *J. Mol. Catal.* **1997**, *124*, 137.
(19) Xu, W.; Dong, J.; Li, J.; Wu, F. *J. Chem. Soc., Chem. Commun.* **1990**, 755.
(20) Kim, M. H.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1993**, *1*, 191.
(21) Matsukata, M.; Nishiyama, N.; Ueyama, K. *Microporous Mater.* **1993**, *1*, 219.
(22) Hari Prasad Rao, P. R.; Matsukata, M. *J. Chem. Soc., Chem. Commun.* **1996**, 1441.
(23) Hari Prasad Rao, P. R.; Ueyama, M.; Matsukata, M. *Appl. Catal.* **1998**, *166*, 97.
(24) Tatsumi, T.; Xia, Q.; Nizamidin, J. *Chem. Lett.* **1997**, 677.
(25) Geobaldo, F.; Bordiga, S.; Zecchina, A.; Gianello, E.; Leofanti, G.; Petrini, G. *Catal. Lett.* **1992**, *16*, 129.
(26) Maache, M.; Janin, A.; Lavalley, J. C.; Joly, J. F.; Benazzi, E. *Zeolites* **1993**, *13*, 419.
(27) Bourgeat Lami, E.; Fajula, F.; Anglerot D.; Des Courieres, T. *Microporous Mater.* **1993**, *1*, 237.
(28) Zecchina, A.; Bordiga, G.; Spoto, G.; Marchese, L.; Petrini, G.; Leofanti, G.; Padovan, M. *J. Phys. Chem.* **1992**, *96*, 4991.
(29) Bellussi, G.; Carati, A.; Clerici, M. G.; Esposito, A. *Stud. Surf. Sci. Catal.* **1991**, *63*, 421.
(30) Khouw, C. B.; Davis, M. E. *J. Catal.* **1995**, *151*, 77.
(31) Tatsumi, T.; Yako, M.; Nakamura, M.; Yuhara, Y.; Tominaga, H. *J. Mol. Catal.* **1993**, *78*, L41.