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Oxidation Activity of Ti-Beta Synthesized by a Dry-Gel Conversion Method

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Ti-beta zeolite was synthesized in the presence of sodium cations by a dry-gel conversion method using tetraethylammonium hydroxide as a structure-directing agent. As evidenced by diffuse reflectance UV spectroscopy, incorporated titianium species were tetrahedrally coordinated in the zeolites and neither anatase-like phase nor hexacoordinated titianium species belonging to an amorphous titanosilicate phase was detected at the sodium content of lower than 1.0 mol%. It was found that the Ti-beta catalysts gave very high H_2O_2 conversion and selectivity in the oxidation of cyclohexene in methanol used as solvent. The C_6-C_8 cyclic alkenes and alkanes reacted faster than corresponding linear alkenes and alkanes, showing the lack of steric impediments in the pores of Ti-beta. Dimethylcyclohexanes were more reactive when tertiary H atoms predominantly occupy the equatorial position than when they occupy the axial position. Ti-beta samples exhibited high activity also for the oxidation of C_6-C_8 cyclic alcohols. © 1998 Academic Press

INTRODUCTION

Titanium silicalites (TS-1 and TS-2) are highly efficient catalysts for the oxidation of a large number of organic substrates, such as alkenes, alcohols, aromatics, and alkanes, using H_2O_2 as oxidant under mild conditions (1). However, the reaction is rather limited to molecules which are able to enter the 10-membered ring channels; for example, cyclic and branched alkanes and alkenes are oxidized much more slowly than the corresponding linear alkanes and alkenes, respectively (2, 3). It is therefore desirable to expand the potential catalytic applications of these materials by synthesizing Ti-containing large-pore zeolites with Ti in the appropriate coordination state.

Recently, a large pore Ti-containing zeolite, Ti-beta, has been hydrothermally synthesized from gels containing tetraethylammonium hydroxide (TEAOH) as a structure directing agent (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, 6). 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). In this conventional synthesis, however, Ti-beta zeolite with SiO_2/Al_2O_3 higher than 200 could not be obtained and the synthesis was always accompanied by a very low zeolite yield (7).

Improved synthesis methods, e.g., cogel method (8), seeding techniques (9, 7), and fluoride method (10) have been developed to obtain the Ti-beta zeolites with high yields. Successful preparation of Ti-beta without the need for Al and alkali cations in the gel was patented by ARCO using benzyl-substituted diquaternary ammonium cation as a novel structure-directing (11). In the crystallization of a variety of zeolites, vapour-phase transport (VPT) method is also an efficient one (12–14), 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 preparations need nonvolatile structure-directing agents. Recently, Rao and Matsukata (15) 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 a certain amount of sodium by the DGC method using TEAOH (16). The product yield was more than 95%.

In this work, we investigate the catalytic activity of Ti-beta zeolite synthesized by a dry-gel conversion method for the oxidation of alkenes, alcohols, and alkanes using aqueous H_2O_2 as the oxidant.

EXPERIMENTAL

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

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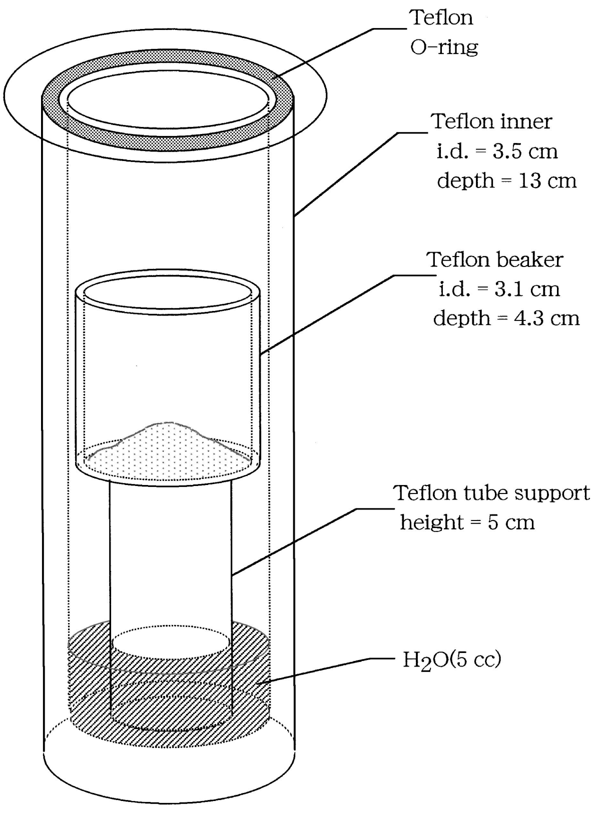


FIG. 1. Apparatus for the synthesis of zeolites by the dry gel conversion method.

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 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 Teflon beaker situated in a Teflon inner (Fig. 1) of a special autoclave, where water (5.0 g) as a source of steam was poured into the bottom. Thermogravimetric (TG) analysis of the dry gel showed that its water content was 25–27 wt%. Most of water contained in the dry gel was that adsorbed from ambient air during grinding; the dry gel before grinding contained 8–9 wt% water.

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 recovered product (6.7 g) 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 resulting Ti-beta zeolite was 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.

By using colloidal silica (ST-40, 40 wt% SiO_2, Nissan), instead of fumed silica, Ti-beta zeolite with higher crystallinity was synthesized. The molar composition of the gel was $SiO_2 : TiO_2 : Al_2O_3 : Na_2O : TEAOH = 310 : 10 : 0.52 : 12 : 135$.

X-ray powder diffraction patterns were collected on a Rigaku Denki RU-200A diffractometer using Cu-Kα radiation. UV-visible spectra (UV-vis) were obtained on a Hitachi 340 spectrophotometer. Thermogravimetric (TG) analysis was carried out in a flow of nitrogen gas on an ULVAC TM-9000 thermal analyzer. SEM micrographs were obtained with a JEOL JSM 5400 microscope equipped with an ED probe.

Catalytic Reactions

The alkene oxidation reactions were conducted at 333 K for 3 h in a glass round-bottom flask (50 ml) fitted with a condenser and a magnetic stirrer. Typically, 16.5 mmol of alkene, 10 ml of solvent, 0.1 g catalyst, and 5 mmol of diluted (31%) hydrogen peroxide were mixed in the flask and heated to the desired temperature under vigorous agitation. The oxidation of alkenes with *tert*-butyl hydroperoxide (TBHP, 69 wt% aqueous solution, Kishida) was conducted at 333 K for 5 h. The oxidation of alcohols was conducted at 338 K. The alkane oxidation reactions were conducted at 373 K for 5 h in an autoclave with a Teflon inner (30 ml). After reaction 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.

RESULTS AND DISCUSSION

Catalyst Characterization

Chemical compositions and crystallinity of Ti-beta samples are given in Table 1 based upon the ICP and XRD measurements. The Ti-beta-DGC synthesized from colloidal silica with a high content of sodium ($Na_2O/SiO_2 = 0.04$) is highly crystallized and used as a reference (100%) of crystallinity. The composition of the gel in the synthesis of Ti-beta-DGC significantly affects the crystallinity of the products. The presence of Na is unfavorable for the synthesis of Ti-beta by the hydrothermal method (4). However, for the DGC method, the presence of certain amount of Na in the gel is necessary. At the Na content of 0.39 mol%, the product was amorphous. On the other hand, when the Na content is too high, the products is not well crystallized (e.g., Sample 8 in Table 1). The amount of Al in the gel also influences the crystallinity of the products. At Al contents lower than 0.16 mol%, only amorphous products are obtained. The high crystallinity of the products can be obtained with the ratios of Na/(Si + Ti + Al) and Al/(Si + Ti + Al) between 0.7 and 1.0 mol% and between 0.16 and 0.80 mol%,

TABLE 1

Results of the Synthesis of Ti-Beta Catalysts

	In gel (mol%)			In zeolite (mol%)				H_2SO_4-washed (mol%)		
Sample no.	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/($T^{IV}+Al$)
1	3.19	0.98	0.16	3.30	0.52	0.12	70	2.32	0.23	0.12
2	3.20	0.68	0.29	3.12	0.64	0.30	81	2.17	0.23	0.12
3	3.18	0.99	0.29	3.12	0.92	0.28	74	2.29	0.22	0.15
4	3.18	0.98	0.29	3.12	1.02	0.27	82	2.66	0.18	0.15
5	3.17	0.98	0.80	3.23	1.04	0.62	85	3.11	0.10	0.49
6	3.18	0.64	0.16	3.44	0.60	0.13	72			
7	3.18	0.98	0.16	3.30	0.66	0.12	80			
8	3.20	1.93	0.29	3.39	1.95	0.30	38			
9	3.18	0.39	0.29		n.d		0			
10	3.18	0.98	0.13		n.d		0			

respectively. Upon treatment of the Ti-beta-DGC samples with 1 *M* H_2SO_4 at room temperature, the Al and Na contents are remarkably decreased and Ti is also slightly lost.

The UV-visible spectra of the calcined Ti-beta synthesized by the DGC method are presented in Fig. 2. 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 generally observed for Ti-substituted molecular sieves (17). The absence of the band between 310 and 350 nm indicates that anatase-like phase is not formed in these samples during crystallization. Sample 8, synthesized in the presence of a large amount of alkali cations ($Na/(T^{IV}+Al) = 1.93\%$), shows a broad shoulder band at 270 nm, which can be attributed to hexacoordinated Ti species belonging to an amorphous titanosilicate phase (5). It has been reported that the presence of alkali cation could prevent titanium from being incorporated into the framework during hydrothermal syntheses (5). In agreement with the conventional hydrothermal synthesis method (7), the existence of Na below 1 mol% does not affect the incorporation of titanium into the framework in the synthesis by the DGC method.

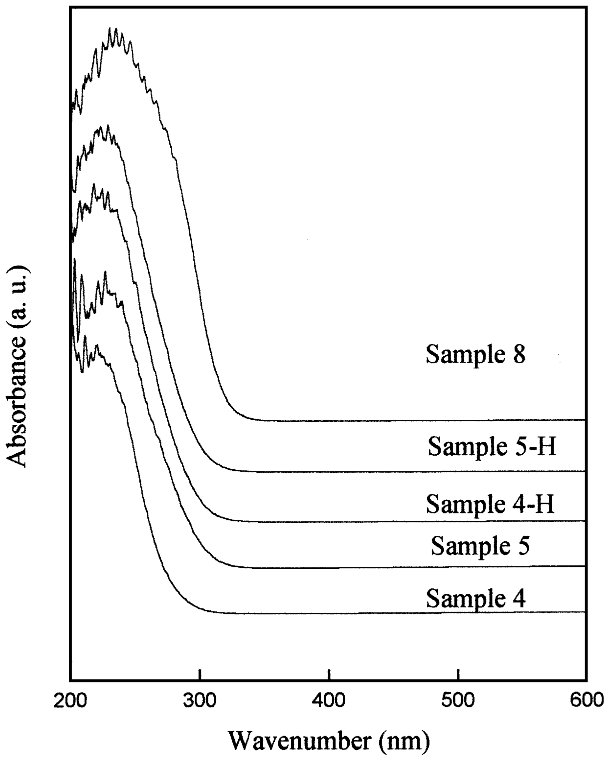


FIG. 2. UV-vis spectra of Ti-beta zeolites. H : H_2SO_4-washed sample.

The particle size of the Ti-beta samples synthesized by the DGC method is rather uniform and no amorphous phase can be found in the samples. The average crystal size of the Samples 1–8 prepared from fumed silica is in the range of 20–40 nm (18), being much smaller than that of the DGC Ti-beta prepared from colloidal silica (ca 100 nm).

Influence of Ti-Beta Composition on its Catalytic Activity in the Oxidation of Cyclohexene

Table 2 shows the catalytic activities of the Ti-beta samples synthesized by the DGC method for the oxidation of cyclohexene with H_2O_2. High cyclohexene conversion and turnover number (TON) with almost 100% selectivity of H_2O_2 to the product is obtained with the calcined Samples 1–7. Because of very high conversion levels it is difficult to meaningfully relate the catalyst performance to the structure and composition of the catalyst. However, the following explanations for the difference in the catalytic performance could be given. Sample 8 with higher Na content exhibits low activity, as was found for TS-1 by Khouw and Davis (19). Another explanation for this low activity is the low crystallinity of Sample 8; Sample 9, which is completely amorphous, shows negligible activity. Slightly low H_2O_2

TABLE 2

Activity of Ti-Beta Catalysts for the Oxidation of Cyclohexene with H_2O_2[a]

Sample no.	Calcined							H_2SO_4-Washed						
	Cyclohexene		Selectivity[c] (%)			H_2O_2(%)		Cyclohexene		Selectivity[c] (%)			H_2O_2(%)	
	Conv.(%)	TON[b]	Epox.	GLYS	CHO	Conv.	Selec.	Conv.(%)	TON[b]	Epox.	GLYS	CHO	Conv.	Selec.
1	96	87	2.6	95	2.9	96	100	86	113	0.2	96	3.9	87	100
2	99	94	0.2	97	3.0	99	100	79	112	0	97	3.2	80	99
3	83	81	1.9	94	3.6	85	98	89	118	0.1	96	3.5	89	99
4	100	98	1.2	96	2.9	100	100	89	107	0.1	97	2.7	98	96
5	100	93	2.6	97	0.6	100	100	99	97	0	97	3.3	100	100
6	96	84	1.4	95	3.6	96	99							
7	96	87	1.4	95	2.8	96	100							
8	69	61	23	72	5.0	76	90							
9	0.8	2.5	10	83	7.0	8	33							

[a] Reaction conditions: Reaction temp. 333 K, reaction time 3 h, 16.5 mmol of cyclohexene, 5 mmol of H_2O_2 (31 wt% in water), 10 ml of methanol (solvent), 0.1 g of catalyst. Cyclohexene conversion is based on H_2O_2.

[b] Moles of products/moles of Ti in the catalyst.

[c] Epox: epoxide, GLYS: glycol and monomethyl glycol ethers, CHO: 2-cyclohexene-1-ol and 2-cyclohexene-1-one.

selectivity for Sample 8 could be related to the presence of hexacoordinate Ti.

By washing with H_2SO_4, the cyclohexene conversion is slightly decreased, except for Sample 3, probably due to the decrease in Ti content by washing. Although the TON of Ti-beta catalysts is increased by washing, the observed TONs do not seem to present the inherent activity due to very high H_2O_2 conversion conditions; before washing the TON could be seriously limited by the almost 100% conversions of H_2O_2. The presence of Al in these catalysts results in the production of glycols, whereas the catalysts with higher Na content exhibit higher selectivity to the epoxide. Without exception, the H_2SO_4-washed Ti-beta catalysts prefer glycols. It should be noted that neither the Na content in the range of about 0.5–1.0 mol% nor the Al content in the range of 0.1–0.6 mol% produces a detrimental effect on the activity and H_2O_2 selectivity in the cyclohexene oxidation.

Solvent Effect on the Activity of Cyclohexene Oxidation

It is known that the choice of the solvent can have a crucial effect on the activity and selectivity in the liquid phase oxidations on titanium silicalites (20–22). The oxidation of cyclohexene is conducted on the Ti-beta samples using several protic and aprotic solvents having different polarity (dielectric constants). These solvents are chosen to form a single phase with the organic substrate and hydrogen peroxide solution, so that mass transfer problems associated with the presence of different liquid phases are avoided.

The influence of nature of solvents is presented in Table 3. It can be seen that the activities observed with

TABLE 3

Influence of Solvents on Conversion and Selectivity of Oxidation of Cyclohexene with H_2O_2 on Ti-Beta[a]

Solvent	Conversion (%)	Selectivity (%)					H_2O_2 (%)	
		Ol[b]	One[c]	Epoxide	Glycols	MGE	Conv.	Selec.
MeOH	100	0.5	2.5	0.1	9.0	88[d]	100	100
EtOH	92	1.1	2.5	0.2	17	78[d]	94	98
t-BuOH	72	3.9	3.8	2.8	78	11[d]	74	98
MeCN	55	5.8	3.4	57	32	0.0	74	78
MeCOMe	63	1.8	0.6	1.8	94	2.0[e]	72	87
MeCOEt	70	3.3	2.0	1.0	93	0.5[e]	74	94

[a] Reaction conditions: Reaction temp. 333 K, reaction time 3 h, 16.5 mmol of cyclohexene, 5 mmol of H_2O_2 (31 wt% in water), 10 ml of solvent, 0.1 g of catalyst (Ti-beta-DGC-5). Cyclohexene conversion is based on H_2O_2.

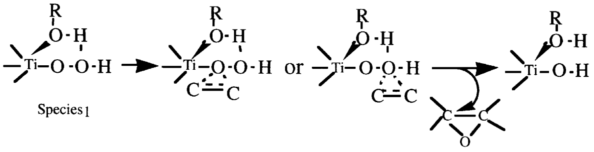
[b] 2-Cyclohexene-1-ol.

[c] 2-Cyclohexene-1-one.

[d] Monoalkyl glycol ethers.

[e] Cyclic ketal formed by reaction of solvent ketone with the glycohols.

protic solvents are higher than those with aprotic ones. Clerici and Ingallina reported that the activity of TS-1 for epoxidation of alkenes is enhanced by the use of protic solvents and ascribed the positive effect of protic solvents to the formation of a cyclic species 1 prior to the coordination of the alkene to the Ti-peroxo complex as follows (20):



SCHEME 1

It was observed that the epoxidation activity of TS-1 decreased in the order MeOH > EtOH > *t*-BuOH as a result of decreasing electrophilicity and increasing steric constraints of species 1 (20). The Ti-beta catalysts exhibited similar dependence in the epoxidation (Table 3), suggesting that a mechanism similar to the one proposed for TS-1 (Scheme 1) is operative for the Ti-beta. It should be noted that the selectivity for allylic oxidation increases in the same order. In the aprotic solvents the epoxidation activity of Ti-beta zeolite is lower than in protic solvents and increases with decreasing dielectric constant of solvent in the order: MeCN < MeCOMe < MeCOEt. Corma *et al.* (22) reported that the activity of epoxidation of 1-hexene over the hydrothermally synthesized Ti-beta zeolite was higher in the aprotic solvent acetonitrile than in protic ones and decreased in the order: MeCN > MeCOMe > MeCOEt. They ascribed that this solvent effect which differs from that for TS-1 is related to the hydrophilicity of the hydrothermally synthesized Ti-beta. The solvent effects obtained in this study which is opposite to those observed by Corma *et al.* suggest that the Ti-beta synthesized by the dry-gel method is relatively hydrophobic, as is the case of TS-1.

The products selectivity in the protic solvents exhibits the same order as Corma *et al.* reported for the oxidation of 1-hexene on hydrothemally synthesized Ti-beta (22). The higher selectivity to the epoxide obtained by using acetonitrile as solvent is explained by decreasing acidity caused by the coordination of the basic acetonitrile molecules and subsequent decrease in the extent of acid-catalyzed secondary reactions.

Epoxidation of Alkenes

The results of the oxidations of cyclic and linear alkenes on the Ti-beta catalyst are summarized in Table 4. The reactivity of alkenes on the Ti-beta catalyst follows a decreasing order: cyclohexene > cycloheptene > cyclooctene ≒ *cis*-3-heptene > *cis*-2-heptene > *cis*-1-heptene > 1-dodecene > cyclododecene.

The reactivity of cyclic alkenes decreases with increasing carbon number. The reactivity of cyclododecene is the lowest, probably due to the low diffusivity of cyclododecene and the corresponding epoxide compared to the diffusivities of the other alkenes or their epoxides in the channels of the beta zeolite. The high reactivity of *cis*-3-heptene and *cis*-2-heptene compared to 1-heptene is in agreement with the previous observations for TS-1 (3, 20) and Ti-beta (6) and can be accounted for by electrophilic character of the attack of active oxygen species. The difference in the reactivities between 1-heptene and 1-dodecene is not so remarkable as is in the case of TS-1. In the latter case, the reactivity significantly decreased with increasing chain length (3). This may be due to the fact that the diffusivity of linear alkene does not remarkably decreases with increasing chain length in the large pore of Ti-beta compared to the medium pore of TS-1.

The efficiency of H_2O_2 was found 100% in the epoxidations of cyclic alkenes over the Ti-beta at 333 K for

TABLE 4

Oxidation of Cyclic Alkenes and Linear Alkenes Using H_2O_2 over Ti-Beta[a]

Alkene	Conversion (%)	Selectivity (%)				H_2O_2 (%)	
		Ol[b]	One[c]	Epoxide	Glycols[d]	Conv.	Selec.
Cyclohexene	100	2.5	0.4	1.2	96	100	100
Cycloheptene	83	1.0	1.1	71	27	83	100
Cyclooctene	73	0.0	0.0	100	0	73	100
Cyclododecene	32	0.0	0.0	100	0	32	100
Cis-3-heptene	74	0.0	0.0	78	22	74	100
Cis-2-heptene	67	0.0	0.0	62	38	67	100
1-Heptene	51	0.0	0.0	57	43	55	96
1-Dodecene	43	0.0	0.0	41	59	50	87

[a] Reaction conditions: Reaction temp. 333 K, reaction time 3 h, 16.5 mmol of alkene, 5 mmol of H_2O_2 (31 wt% in water), 10 ml of methanol (solvent), 0.1 g of catalyst (unwashed sample 4). Alkene conversion is based on H_2O_2.

[b] 2-Cyclohexene-1-ol.

[c] 2-Cyclohexene-1-one.

[d] Glycols contain methyl glycol ethers.

TABLE 5

Oxidation of Cyclic Alkene with TBHP over Ti-Beta[a]

Alkene	Conversion (%)	Selectivity (%)				TBHP (%)	
		Ol[b]	One[c]	Epoxide	Glycols[d]	Conv.	Selec.
Cyclohexene	36	0.4	3.6	9.7	86	40	90
Cycloheptene	18	0.6	1.4	90	8.0	30	60
Cyclododecene	3.6	0.0	0.0	100	0.0	20	18

[a] Reaction conditions: Reaction temp. 333 K, reaction time 5 h, 16.5 mmol of cyclic alkene, 5 mmol of TBHP (*tert*-butyl hydroperoxide) 69 wt%, 10 ml of methanol (solvent), 0.1 g of catalyst (unwashed sample 1). Alkene conversion is based on TBHP.

[b] 2-Cyclohexene-1-ol.

[c] 2-Cyclohexene-1-one.

[d] Glycols contain monomethyl glycol ethers.

3 h. Although the reactivity of cyclic alkenes on Ti-beta showed the decreasing order: cyclohexene > cycloheptene > cyclooctene, the epoxide selectivity showed the increasing order: cyclohexene < cycloheptene < cyclooctene. For cyclohexene, the ring-opening products of the epoxide were obtained almost exclusively. In contrast, for cyclooctene quantitative conversion to epoxide was attained, in agreement with the results reported by Dartt and Davis for hydrothermally synthesized Ti-beta catalysts (23). Cycloheptene gave rise to intermediate selectivity for epoxide. These results suggest that bulkier alkene oxides are prevented from solvolysis which requires bulkier transition state in the sterically resistricted pore of Ti-beta. For the linear alkenes, the epoxide selectivity is in the order: *cis*-3-heptene > *cis*-2-heptene > 1-heptene > 1-dodecene (6). These results indicate that less sterielly demanding terminal epoxides get easier access to the acid site in the pore of Ti-beta than internal epoxides.

There is another explanation for the increasing selectivity for epoxides with increasing molecular size. It is conceivable that the large molceules which cannot effectively diffuse into the micropores react on the external surface or pore mouth of the catalyst. Since Al^{3+} plays an important role in nucleation of the beta phase, Al^{3+} could be present mainly in the micropores and not on the external surface. If this is the case, the cyclic alkenes with large size might be only epoxidized without following acid catalyzed hydration.

Epoxidation of Alkenes with TBHP

TBHP was shown to be ineffective for oxidation on TS-1 (24), owing to the difficulty of TBHP to diffuse and to coordinate the Ti sites inside the narrow channels of the MFI structure. The steric restrictions could be overcome when Ti-beta with larger pore dimensions is used as catalysts.

The results of the epoxidation of cyclic alkenes on the Ti-beta using TBHP as oxidant are summarized in Table 5. The reactivity of cyclic alkenes and TBHP selectivity decrease with increasing molecules size, cyclohexene > cycloheptene > cyclododecene. We assume a similar mechanism is operative in the oxidation of alkenes with H_2O_2 and TBHP. The higher conversion was obtained with H_2O_2 than with TBHP and the TBHP selectivity is lower than the H_2O_2 selectivity (Tables 4 and 5). This difference is increased with increasing molecule size of cyclic alkenes, suggesting that steric restrictions inside the pores of Ti-beta are enhanced when using a bulkier oxidant such as TBHP, which is in agreement with the results obtained by Corma *et al.* for oxidation of alkenes over hydrothermally synthesized Ti-beta with TBHP (5). Obviously the transition state involving the Ti-OOR and alkene must be bulkier when TBHP is used as oxygen donor.

Oxidation of Cyclic Alcohols

We have studied the oxidation of cyclic alcohols on the Ti-beta catalyst using hydrogen peroxide as oxidant. These 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 6, the reactivity of cyclic alcohols followed the decreasing order: cycloheptanol > cyclooctanol > cyclohexanol > 3-methylcyclohexanol. The methyl substituent in cyclohexanol causes a serious hindrance to the coordination of the alcoholic group to the active site of Ti-beta. The high

TABLE 6

Oxidation of Cyclic Alcohol Using H_2O_2 over Ti-Beta[a]

Cyclic alcohol	Conversion (%)	H_2O_2 (%)	
		Conv.	Selec.
Cyclohexanol	44	80	55
Cycloheptanol	59	80	74
Cyclooctanol	48	80	61
3-Methylcyclohexanol	7.3	70	11

[a] Reaction conditions: Reaction temp. 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 (unwashed sample 3). Alcohol conversion is based on H_2O_2.

TABLE 7

Oxidation of Normal and Branched Alkanes Using H_2O_2 over Ti-Beta[a]

Alkane	Alkane		Selectivity (%)							H_2O_2 (%)	
	Conv.(%)	TON	1-ol	2-ol	3-ol	4-ol	2-one	3-one	4-one	Conv.	Selec.
n-Hexane	5.0	10	0.0	49	31	—	12	9.0	—	89	6.8
3-Methylpentane	6.4	12	0.0	52	35		13			89	9.2
3,4-Dimethylhexane	3.2	6.8	0.0	19	45		13			89	3.6
n-Heptane	6.0	13	0.0	32	29	17	12	7.9	3.3	90	8.3
n-Octane	6.0	12	0.0	23	25	34	6.6	5.2	6.8	90	8.0

[a] Reaction conditions: Reaction temp. 373 K, reaction time 5 h, 18.7 mmol of alkane, 9.3 mmol of H_2O_2 (31 wt% in water), 10 ml of methanol (solvent), 0.1 g of catalyst (unwashed sample 7). Alkane conversion is based on H_2O_2.

conversion of cycloheptanol and cyclooctanol seems to be due to intrinsic high reactivity unaffected by the steric restriction imposed by the pore structure.

Oxidation of Linear and Branched Alkanes

Ti-beta samples are found active in oxidation of alkanes with H_2O_2. Oxidation occurs at tertiary or secondary C-H bonds; no terminal oxidation products being detected (Table 7). The reactivity of linear and branched alkanes on the Ti-beta and the selectivity of H_2O_2 show the following order: 3-methylpentane > *n*-heptane = *n*-octane > *n*-hexane > 3,4-dimethylhexane. There are one tertiary C-H bond and four secondary C-H bonds in the 3-methylpentane. The specific selectivity for tertiary C-H bond oxidation (product selectivity for tertiary C-H bond oxidation/number of tertiary C-H bond, $35/1 = 35$) is higher than that for secondary C-H bond oxidation ($65/4 = 16$), indicating that tertiary C-H bond is more reactive than secondary C-H bond. It has been reported that TS-1 shows higher activity for *n*-hexane oxidation than for branched C_6 alkanes, such as 3-methylpentane, for which diffusion is restricted through the medium pores of the MFI structure (2, 25). It is also known that the reactivity of linear alkanes on TS-1 decreases in the order: hexane > heptane > octane, which is explained by decreasing diffusivity of these linear alkanes with increasing chain length (2). In contrast, all these molecules probably diffuse relatively easily through the channels of the large pore Ti-beta, and therefore the activity of this catalyst is not determined by diffusion through the pores but by the intrinsic reactivity of the alkanes. Low reactivity of 3,4-dimethylhexane would be due to the two methyl groups causing a steric restriction against the access of the molecules to the active sites.

Oxidation of Cyclic Alkanes

Table 8 shows the results obtained from the oxidation of cyclic alkanes with different molecular sizes on the Ti-beta using H_2O_2 as the oxidant. The reactivity shows a decreasing order: cycloheptane ≒ cyclooctane > methylcyclohexane > cyclohexane > cyclododecane.

Cyclic alkanes are converted to the corresponding cyclic alcohols and ketones. The reactivity of cyclododecane is the lowest, probably due to the large molecular size, preventing cyclododecane molecules from diffusing into the channels

TABLE 8

Oxidation of Cyclic Alkanes Using H_2O_2 over Ti-Beta[a]

Cyclic alkane	Cyclic alkane		Selectivity (%)		H_2O_2 (%)	
	Conv.(%)	TON	Ol	One	Conv.	Selec.
Cyclohexane	22	47	77	23	91	30
Methylcyclohexane	26	49	96[b]	4.0[c]	90	31
Cycloheptane	34	77	65	35	90	51
Cyclooctane	34	76	67	34	90	50
Cyclododecane	4.2	9.8	68	32	95	5.9

[a] Reaction conditions: Reaction temp. 373 K, reaction time 5 h, 18.7 mmol of cyclic alkane, 9.3 mmol of H_2O_2 (31 wt% in water), 10 ml of methanol (solvent), 0.1 g of catalyst (unwashed sample 7). Cyclic alkane conversion is based on H_2O_2.

[b] (40% of 1-methylcyclohexanol + 19% 2-methylcyclohexanol + 22% 3-methylcyclohexanol + 15% 4-methylcyclohexanol).

[c] (2% 2-methylcyclohexanone + 2% 4-methylcyclohexanone).

TABLE 9

Oxidation of Methylcyclohexane Using H_2O_2 over Ti-Beta[a]

Dimethylcyclohexane	Dimethyl-cyclohexane Conv.(%)	Dimethyl-cyclohexane TON	Selectivity (%) 1,3-DM-1-ol	3,5-DM-1-ol	2,4-DM-1-ol	2,6-DM-1-ol	3,5-DM-1-one	2,4-DM-1-one	H_2O_2 (%) Conv.	H_2O_2 (%) Selec.
cis-1,3-dimethylcyclohexane	15	33	24	33	16	4.8	11	11	88	22
trans-1,3-dimethylcyclohexane	46	87	87		7.4			5.0	89	55
			1,2-DM-1-ol	2,3-DM-1-ol	3,4-DM-1-ol	2,3-DM-1-one		3,4-DM-1-one		
cis-1,2-dimethylcyclohexane	36	72	72	9.7	7.0	4.9		6.0	87	47
trans-1,2-dimethylcyclohexane	13	25	9.9	60	18	6.6		5.9	89	17

[a] Reaction conditions: Reaction temp. 373 K, reaction time 5 h, 18.7 mmol of alkane, 9.3 mmol of H_2O_2 (31 wt% in water), 10 ml of methanol (solvent), 0.1 g of catalyst (unwashed sample 7). Dimethylcyclohexane conversion is based on H_2O_2. DM: dimethylcyclohexane.

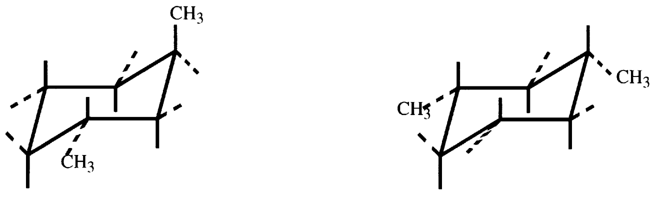
of the zeolites. In contrast, the sizes of the molecules of cyclooctane, cycloheptane, methylcyclohexane and cyclohexane are relatively smaller and therefore their conversions may be determined by the intrinsic reactivities of the molecules. The conversion of methylcyclohexane is higher than that of cyclohexane, due to tertiary carbons being more reactive than secondary carbons.

The reactivity and H_2O_2 selectivity are much lower for the linear alkanes than for the cyclic alkanes when the alkanes with the same carbon number are compared. Oxidation of linear alkanes occurred at secondary C-H bonds and not at the terminal carbons as shown in Table 7. The reason is not clear. We only speculate that the terminal methyl groups in linear alkanes could be relatively easy to approach the sterically crowded active site resulting in the obstruction for secondary C-H bonds in gaining access to the active site in the pores of Ti-beta. For the oxidation of alkanes over TS-1, the linear alkanes showed much higher reactivity than the cyclic alkanes, due to the small channel size of the 10-membered ring zeolite (2).

Influence of Steric Factor in Oxidation of Dimethylcyclohexanes

To investigate the effect of the methyl substituents on the reactivity, a comparison was made among the reactivities of 1,2- and 1,3-dimethylcyclohexanes. The results obtained from the oxidation of *cis*- and *trans*-isomers on the Ti-beta zeolites are presented in Table 9. The reactivity follows the order: *trans*-1,3-dimethylcyclohexane > *cis*-1,2-dimethylcyclohexane > *cis*-1,3-dimehtylcyclohexane > *trans*-1,2-dimethylcyclohexane.

The stable conformation of each dimethylcyclohexane isomer is shown in Fig. 3. For *trans*-1,3- and *cis*-1,2-



trans-1,3-dimethylcyclohexane *cis*-1,3-dimethylcyclohexane

trans-1,2-dimethylcyclohexane *cis*-1,2-dimethylcyclohexane

FIG. 3. Stable conformation of dimethylcyclohexane isomers.

TABLE 10

Reactivity of Tertiary and Secondary C-H Bonds of Dimethylcyclohexanes over Ti-Beta[a]

Dimethylcyclohexane	Tertiary C-H (Ti^{-1} h^{-1})	Secondary C-H (Ti^{-1} h^{-1})
cis-1,3-dimethylcyclohexane	0.79	0.63
trans-1,3-dimethylcyclohexane	7.60	0.27
cis-1,2-dimethylcyclohexane	5.20	0.50
trans-1,2-dimethylcyclohexane	0.25	0.56

[a] Reactivity of tertiary and secondary C-H bonds was calculated from the data in Table 9: TON ∗ selectivity/reaction time/number of tertiary or secondary C-H bonds (Ti^{-1} h^{-1}).

dimethylcyclohexanes, there exists a pair of conformations. In either conformation, only one methyl group occupies the axial position. In contrast, for *cis*-1,3- and *trans*-1,2-dimethylcyclohexanes both methyl groups can occupy the equatorial position in the stable conformation. All these molecules probably diffuse relatively easily through the channels of the large pore Ti-beta, and therefore the catalytic activity is not determined by diffusion through the pores, but their methyl substituents and the position of tertiary C-H bond produce steric effects on the reactivity of the alkanes.

There are two tertiary C-H bonds (one axial and one equatorial) and eight secondary C-H bonds (4 axial and 4 equatorial) in *trans*-1,3-dimethylcyclohexane. As shown in Table 10, in *trans*-1,3-dimethylcyclohexane the specific reactivity of tertiary C-H bond (product from tertiary C-H bond oxidation/number of tertiary C-H bond, $87 * 0.87/5/2 = 7.6$ Ti^{-1} h^{-1}) is much higher than that of secondary C-H bond ($87 * 0.124/5/8 = 0.27$ Ti^{-1} h^{-1}). In *cis*-1,3-dimethylcyclohexane, the specific reactivity of tertiary C-H bond ($33 * 0.24/5/2 = 0.79$ Ti^{-1} h^{-1}) is similar to that of secondary C-H bond ($33 * 0.76/5/8 = 0.63$ Ti^{-1} h^{-1}). The reactivity of tertiary C-H bond is much smaller in *cis*-1,3-dimethylcyclohexane than in its *trans* isomer. In the former both tertiary C-H bonds which should be intrinsically reactive are forced to occupy the axial position in the stable conformation. The groups in the axial position are supposed to experience more difficulty in approaching the active site in the pore than those in the equatorial position and this steric restriction would account for the low reactivity of tertiary C-H bonds in *cis*-1,3-dimethylcyclohexane.

The specific reactivity of tertiary C-H bond is also higher in *cis*-1,2-dimethylcyclohexane than in *trans*-1,2-dimethylcyclohexane. While in the former one tertiary C-H bond would occupy the equatorial position and the other the axial position, in the latter both tertiary C-H bonds would be forced to occupy the axial position, leading to the low reactivity. It is noticeable that tertiary C-H bonds in *cis*-1,2-dimethylcyclohexane exhibit slightly lower reactivity (5.2 Ti^{-1} h^{-1} vs 7.6 Ti^{-1} h^{-1}) and selectivity (72% vs 87%) than those in *trans*-1,3-dimethylcyclohexane. This might be due to the presence of the equatorial methyl group in the 2-position, causing some hindrance to the access of the equatorial C-H bond to the active site.

CONCLUSIONS

The large-pore beta zeolite containing Ti have been synthesized by the dry-gel conversion method in the presence of sodium cations using TEAOH as the structure directing agent. The hexacoordinated titianium species belonging to an amorphous titanosilicate phase was not observed in the UV-visible spectra when the sodium content is lower than 1.0 mol%.

The Ti-beta samples proved to be excellent catalysts for oxidation of alkenes. The Ti-beta showed higher activity for epoxidation of alkenes in the protic solvents such as methanol in a similar maner to TS-1. The reactivity of alkenes on the Ti-beta catalyst followed a decreasing order: cyclohexene > cycloheptene > cyclooctene ≒ *cis*-3-heptene > *cis*-2-heptene > *cis*-1-heptene > 1-dodecene > cyclododecene; 100% H_2O_2 selectivity was obtained in the oxidation of cyclic alkenes. The Ti-beta showed high oxidation activity also for the oxidation of C_6-C_8 cyclic alcohols.

Cyclic alkanes showed much higher reactivity than linear alkanes with the same carbon number. The reactivity of dimethylcyclohexanes followed the order: *trans*-1,3-dimethylcyclohexane > *cis*-1,2-dimethylcyclohexane > *cis*-1,3-dimehtylcyclohexane > *trans*-1,2-dimethylcyclohexane. Dimethylcyclohexanes with tertiary H atoms in the equatorial position in the stable conformation are found more reactive than those with tertiary H atoms forced in the axial position.

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