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RESEARCH NOTE

Direct Formation of Pinacols from Olefins over Various Titano–Silicates

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The epoxidation and successive pinacol formation of tri- and tetraalkyl-substituted olefins using Ti-β/H_2O_2/H_2O as the catalytic system has been investigated. Aluminum-free Ti-β exhibits better activity and pinacol selectivity than TS-1, TS-2, Ti–MCM-22, and mesoporous Ti–MCM-41. Pinacol (*vic*-diol) is obtained as the major product with small amounts of the side products pinacolone, alcohol (via hydration), and oligomers. The conversion and pinacol selectivity increase with an increase in reaction temperature and time. The change in product distribution with reaction time over Ti-β shows that the epoxide is the initial product which undergoes a secondary reaction to give pinacol as the major product. The conversion and H_2O_2 selectivity decrease with the bulkiness of the substituents at the C=C bond but the selectivity of pinacol is not significantly affected. The reactivity of cyclic 1-methyl-1-cyclohexene is considerably lower than that of the corresponding open-chain analogue 2-methyl-2-butene. The symmetrical tetramethyl-substituted 2,3-dimethyl-2-butene led to the formation of small amount of dimers over medium-pore titanium silicates TS-1, TS-2, and Ti–MCM-22. The epoxidation of these substituted olefins proceeded more rapidly when using acetonitrile as a cosolvent than under triphase conditions. Mechanistically, the primary epoxide product undergoes acid-catalyzed nucleophilic ring opening by H_2O molecules to give pinacol.

INTRODUCTION

Selective oxidation and epoxidation plays a major role both in industry and in the laboratory for the synthesis of many useful organic building blocks in total synthesis. Thus, one can design the required product by taking advantage of the highly reactive oxirane ring (epoxides) and choosing the right conditions to promote reactions, such as isomerization, condensation, and nucleophilic substitution. For example, styrene epoxide undergoes nucleophilic substitution with aniline over zeolite HY (1) and α-pinene oxide isomerizes to campholenic aldehyde over Ti-β (2). In our study, pinacol (2,3-dimethyl-2,3-butane diol) has been prepared in one pot by the initial epoxidation of the corresponding olefin followed by nuclophilic reaction of the epoxide with H_2O. The name pinacol denotes *vic*-diols with four alkyls groups; more specifically, *vic*-diol with four methyl groups is called pinacol. Pinacol is an important starting material for synthesizing compounds such as pinacolone (*tert*-butyl methyl ketone by the well-known pinacol–pinacolone rearrangement) and pinacolone oxime (by ammoxidation). These compounds are useful intermediates in the production of pesticides, pharmaceuticals, fragrances, photographic chemicals, and crop-protection chemicals (3, 4). The conventional pinacol synthesis is by the hydrolysis of epoxides catalyzed by either a base or an acid, such as perchloric acid (5). Pinacols are also directly synthesized from olefins by reagents such as OsO_4 and alkaline $KMnO_4$ that add two hydroxyl groups to a C=C bond (6). The main drawback of these reagents is that OsO_4 is not only expensive but also highly toxic. Furthermore, the use of alkaline $KMnO_4$ is also limited, as it leads to oxidation of glycols (7, 8). Another strategy for making 1,2-diols is the reduction of aldehydes and ketones with active metals, such as sodium, magnesium, or aluminum (9), but it leads to many side products due to coupling reactions.

Over the course of a decade extensive research has been carried out to replace these stoichiometric reagents with reusable heterogeneous catalysts that are more environmentally friendly. Titanium silicalite and its combination with the clean oxidant H_2O_2 is employed in several chemical industries. Clerici *et al.* compared the reactivity of small olefins such as butenes and pentenes in the epoxidation with hydrogen peroxide over TS-1 (10, 11). Relevant to the present study is the uncatalyzed epoxidation of 2,3-dimethyl-2-butene with molecular O_2 at high temperature reported by Waldmann *et al.* (12). However, the synthesis of pinacol using heterogeneous oxidizing agents such as titanium-silicate and hydrogen peroxide in liquid-phase conditions has not been reported. In this paper, reactivity and pinacol selectivity has been studied for various trialkyl- and tetraalkyl-substituted olefins using Ti-β/H_2O_2 and water as reaction medium (a triphase system). Also,

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reaction parameters such as temperature, reaction time, and the activity of various zeolites have been studied in detail using 2,3-dimethyl-2-butene. For comparison, the epoxidation of different olefins has been carried out using acetonitrile in a two-phase system.

EXPERIMENTAL

Aluminum-free Ti-beta was synthesized in basic medium (pH of 12.5) by modifying a procedure found in the literature (13). The titanoperoxo complex was formed by the addition of $Ti(OBu)_4$ and H_2O_2, which was added to TEAOH under vigorous stirring. Then the required amount of precipitated Nipsil VN-3 silica was added and the stirring was continued for a few hours. Finally, 3% of dealuminated seed crystals was added and the crystallization was conducted at 413 K in a PTFE-lined stainless steel 150-ml autoclave under tumbling (60 rpm). The gel composition was SiO_2:0.025 TiO_2:0.337 H_2O_2:0.55 TEAOH:6.6 H_2O. After the crystallization, the contents were centrifuged and extensively washed with distilled water. The aluminum-containing Ti–Al-β material was synthesized using Al $(NO_3)_3 \cdot 9\ H_2O$ from the gel composition SiO_2:0.0044 Al_2O_3:0.337 H_2O_2:0.55 TEAOH:16 H_2O. The as-synthesized materials were dried at 373 K and calcined in a flow of O_2 for 12 h at 793 K. The calcined Ti-β samples thus obtained were thoroughly characterized by XRD, FTIR, and UV–vis spectroscopies and surface area measurements. TS-1 and TS-2 were synthesized according to the literature (14, 15). In a typical synthesis of TS-1, 42 g of tetraethyl orthosilicate was hydrolyzed with 67.7 g of tetrapropylammonium hydroxide (20% aqueous, Aldrich) with vigorous stirring for 2 h. Then, 2.19 g of $Ti(OBu)_4$ in anhydrous isopropanol and 54 g of water were added and the clear solution was crystallized at 443 K for 30 h under static condition. In the case of TS-2, tetrabutylammonium hydroxide was used and the crystallization was carried out at 443 K for 72 h under static conditions. Ti–MCM-22 was prepared according to the literature (16) using fumed silica (Cab-o-sil-M7D), tetrabutyl orthotitanate (TBOT), boric acid, and piperidine as a structure-directing agent. The mesoporous Ti–MCM-41 was also synthesized according to the reported procedure (17).

The catalytic reactions were carried out using a glass reactor fitted with a water condenser through which ice-cold water was passed. The reaction mixture was vigorously stirred using a magnetic stirrer. A typical reaction involved 10 mmol of substrate, 10 mmol of H_2O_2, 20 wt% catalyst (Ti-β, Si/Ti = 43) with respect to substrate, and 10 ml of water or acetonitrile. For triphase reactions involving water as a dispersion medium, the reaction products are homogenized using the solvent acetone and the reaction products were analyzed by using a capillary gas chromatograph (Shimadzu 14A, OV-1 columns with flame ionization detectors). The products were identified with authentic samples and GC-MS splitting patterns, in combination with thin-layer and column chromatography techniques and ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

Activity of Various Titanium–Silicates

Table 1 shows the reactivity of 2,3-dimethyl-2-butene to 2,3-dimethyl-2,3-butane diol (pinacol) with H_2O_2 over a range of catalysts such as TS-1, TS-2, Ti–MCM-22 (medium-pore zeolites), Ti-β (large-pore zeolite), and Ti–MCM-41 (mesoporous). As our objective is to make pinacol in a single step, the reaction has been carried out using water as a dispersion medium (triphase). As expected, pinacol is formed selectively with the coexistence of a small amount of the primary epoxide product for all the catalysts, immaterial of their activity. The large-pore Ti-β(Si/Ti = 43; crystal size, 0.5–1 μm) exhibits better activity and selectivity for pinacol than the other zeolites studied. However, since Ti-β is partly acidic, acid-catalyzed side products are formed, such

TABLE 1

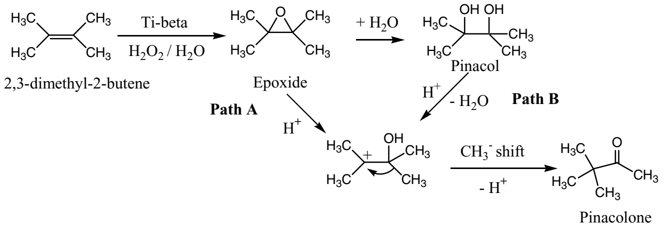
Formation of Pinacol over Various Titanium–Silicates[a]

Entry	Catalyst	Conv. (mol%)	H_2O_2 sel. (%)	Product selectivities (%) Epoxide	Pinacol	Pinacolone	DMB[b]	Others
1	Ti-β (43)[c]	55.3	80.1	1.3	92.9	1.9	4.3	0.5
2	Ti–Al-β (40)	51.2	76.5	1.1	82.6	3.7	15.6	0.4
3	TS-1 (33)	39.2	61.5	3.9	88.0	1.3	1.0	5.9
4	TS-2 (46)	21.2	57.0	4.0	83.6	1.2	1.9	9.0
5	Ti–MCM-22 (51)	22.6	54.5	3.4	86.0	2.0	5.4	5.1
6	Ti–MCM-41 (50)	48.2	65.0	1.6	96.3	1.1	0.7	0.3

[a] Reaction conditions: 10 mmol of 2,3-dimethyl-2-butene; 10 mmol of H_2O_2 (31 wt% aqueous solution); catalyst, 20 wt% with respect to substrate; 5 ml water as a dispersion medium; temperature, 333 K; and reaction time, 6 h.

[b] DMB is 2,3-dimethyl-2-butanol and "others" include oligomers.

[c] The figures in the parentheses represent Si/Ti ratios.



SCHEME 1

as pinacolone (*tert*-butyl methyl ketone via acid-catalyzed rearrangement), 2,3-dimethyl-2-butanol (via hydration of olefin), and small amounts of oligomers. The various products formed in this reaction are depicted in Scheme 1. Though the activities is of Ti-β and Ti–Al-β (Si/Ti $=$ 40; crystal size, 1 μm) are similar, there is a marked difference in the amount of acid-catalyzed products formed; in particular, Ti–Al-β produces a large amount of 2,3-dimethyl-2-butanol via acid-catalyzed hydration of the reactant olefin.

Entries 3–5 (Table 1) show the reactivity and pinacol selectivity over the medium-pore TS-1, TS-2, and Ti–MCM-22 catalysts. The activity of TS-1, with 10-membered ring pore openings, is considerably lower than that of Ti-β, which has large 12-membered ring pore openings. Thus, the difference in activity between the medium-pore TS-1 (Si/Ti $=$ 33) and large-pore Ti-β (Si/Ti $=$ 43) may be due to the diffusion limitation of 2,3-dimethyl-2-butene exerted by medium-pore zeolites, although the former contains more titanium. Furthermore, the activity of TS-2 (Si/Ti $=$ 46) is only one-half that of TS-1, although there is not much difference in their crystallographic structure. The lower activity of TS-2 suggests that the higher Si/Ti ratio coupled with the large particle size (TS-1 and TS-2 crystal sizes are 0.1–0.2 and 2–3 μm, respectively) and the disordered environment around Ti^{IV} species also influence the reactivity. The above results clearly suggest that the morphology of the catalysts and the diffusion of reactants and products play an important role in addition to the pore size of these titano-silicates. The observed activities of TS-2 and Ti–MCM-22 (Si/Ti $=$ 50; crystal size, 0.2–0.5 μm) are similar. All these medium-pore titanium-silicates yield pinacol as the major product, but a small amount of oligomers (particularly dimers) is formed over these zeolites. The mesoporous Ti–MCM-41 (Si/Ti $=$ 51; crystal size, 0.2–0.5 μm) shows good activity and the best selectivity of 96.3% with negligible side products. Furthermore, Ti-β and Ti–MCM-41 show higher H_2O_2 selectivity than the medium-pore titanium-silicates. Thus, the observed activities of the large-pore, medium-pore, and mesoporous catalysts clearly suggest that diffusion of reactants and products controls the rate of reaction and therefore Ti-β was used for further study.

Effect of Reaction Temperature and Time

The influence of temperature on activity and product distribution is presented in Fig. 1 for large-pore Ti-β; separate experimental runs were carried out for each point of the graph in order to get a better mass balance. The temperature has a marked effect on the conversion of the bulky 2,3-dimethyl-2-butene. As expected, the reactivity of 2,3-dimethyl-2-butene increases with temperature while the selectivity to pinacol increases from 87 to 92%. Since even in the absence of aluminum the Ti-β is partially acidic due to the presence of structural defects as well as a large number of silanol groups, it gives rise to acid-catalyzed reactions, such as hydration and rearrangement. Pinacolone, ultimately the most useful product in this reaction, does not increase considerably with temperature, since the Brønsted acid strength is not strong enough for the facile pinacol-to-pinacolone rearrangement. The hydration of 2,3-dimethyl-2-butene to 2,3-dimethyl-2-butanol increases from 4 to 5.1% at 333 K. In Fig. 1 "others" refers to a mixture of epoxides, pinacolone, and oligomers (formed in negligible amounts over large-pore Ti-β). The H_2O_2 selectivity increases slightly with temperature; this is mainly due to the relatively easy diffusion of bulky 2,3-dimethyl-2-butene at high temperature, leading to the increased conversion. As the temperature increases, the epoxide is almost completely converted to pinacol.

Figure 2 exhibits the effect of reaction time on conversion and selectivity of the various products. Pinacol is the major product throughout the course of the reaction and the epoxide selectivity in the first hour is 4.5%, which gradually decreased to 1.3% after 6 h. The selectivity of pinacol increased slightly with time and ranged between 86 and 92%. Thus, the primary epoxide product readily undergoes cleavage to the 1,2-diol (pinacol), possibly due to steric crowding of the four-methyl substituents attached to the oxirane ring as well as to the presence of a large excess of water as a dispersion medium. The acid-catalyzed hydration of

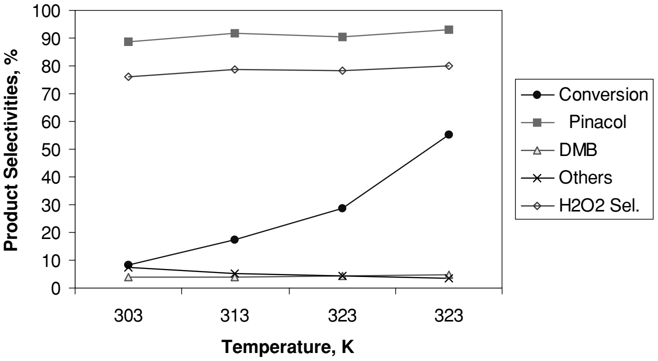


FIG. 1. Reactivity of 2,3-dimethyl-2-butene and product selectivity over Ti-β at different temperatures using H_2O_2 as oxidant and water as reaction medium.

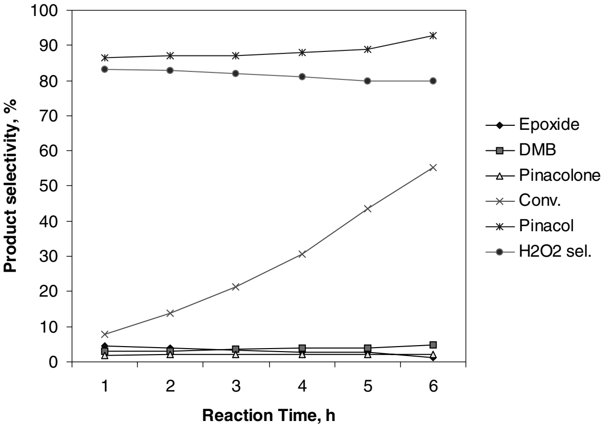


FIG. 2. Distribution of various products with reaction time over a Ti-β/H_2O_2/H_2O catalytic system.

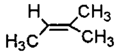
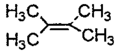
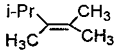
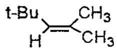
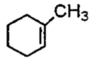
2,3-dimethyl-2-butene also increased slightly with time, to 4.7%. The selectivity of H_2O_2 dropped slightly as the reaction progressed.

Reactivity of Various Tri- and Tetraalkyl-Substituted Olefins over Ti-β

The rate of oxidation is generally dependent on the olefin, i.e., the number and electronic properties of the substituents attached to the olefinic double bond. The observed reactivity and pinacol selectivity of various olefins with the catalytic system Ti-β/H_2O_2/H_2O are given in Table 2. Among the different substrates studied, 2-methyl-2-butene with three methyl substitutents attached to the olefinic double bond showed the highest activity for epoxidation and pinacol formation. Entries 2–4 show the effect of methyl, isopropyl, and *tert*-butyl substituents on the olefinic double bond, respectively. The reactivity of 2,3-dimethyl-2-butene (entry 2) in which four methyl groups are attached to the double bond was less than that observed for 2-methyl-2-butene. When one of the methyl groups in 2,3-dimethyl-2-butene was replaced by an *iso*propyl substitutent, the activity decreased remarkably (entry 3). Similarly, the presence of a *tert*-butyl substituent decreased the reactivity considerably even when the double bond was triply substituted (entry 4). However, the pinacol was obtained in a narrow selectivity range (86–92%). In addition to the normal acid-catalyzed products pinacolone and alcohol, the bulky olefins give appreciable amounts of oligomers. It is generally expected that the rate of reaction should increase with the number of alkyl substituents since they increase the electron density of the double bond. However, the observed reactivity follows the order 2-methyl-2-butene > 2,3-dimethyl-2-butene > 2,3,4-trimethyl-2-pentene > 2,4,4-trimethyl-2-pentene. The titanium-silicate, as an epoxidation catalyst characterized by electrophilic character, should give the reverse order and this order disagrees with what would be expected for the epoxidation with peracids and other electrophilic oxidizing agents (18). This must be due to the steric constraints imposed by the alkyl substitutents at the double bond, which would play a major role in epoxidation and subsequent pinacol formation. Entry 5 exhibits the reactivity of cyclic 1-methyl-1-cyclohexene, which is considerably less reactive than its open-chain analogue 2-methyl-2-butene, probably due to steric hindrance. In addition to epoxidation, 1-methyl-1-cyclohexene also gives a small amount of allylic

TABLE 2

Reaction of Tri- and Tetraalkyl-Substituted Olefins over Ti-β under the Triphase Conditions[a]

Entry	Substrate	Conv. (mol%)	H_2O_2 sel. (%)	Product selectivities (%)				
				Epoxide	Pinacol	Pinacolone	Alcohol[b]	Others
1[c]		60.9	79.0	5.1	89.5	2.9	2.1	0.5
2		55.3	80.1	1.3	92.9	2.1	4.5	0.5
3		39.1	49.7	1.6	89.0	1.5	3.2	4.7
4		23.3	40.1	2.1	87.7	1.9	3.9	5.5
5		26.8	48.2	3.3	86.1	—	—	10.6[d]

[a] Reaction conditions: 10 mmol of substrate; 10 mmol of H_2O_2 (31 wt% aqueous solution); Ti-β, 20 wt% with respect to substrate; 5 ml water as dispersion medium; temperature, 333 K; and reaction time, 6 h.

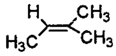
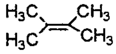
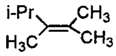
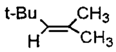
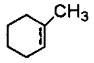
[b] Corresponding alcohol produced via hydration of olefin and "others" include oligomers.

[c] The reaction was carried out in a closed stainless steel reactor (Parr-type reactor), as the substrate has a low boiling point (boiling point 48°C).

[d] Mixture of allylic oxidation products.

TABLE 3

Reaction of Various Tri- and Tetraalkyl-Substituted Olefins over Ti-β Using Acetonitrile Cosolvent[a]

Entry	Substrate	Conv. (mol%)	H_2O_2 sel. (%)	Product selectivities (%)				
				Epoxide	Pinacol	Pinacolone	Alcohol[b]	Others
1[c]		42.5	44.5	48.1	43.5	1.1	1.3	3.0
2		38.0	39.0	28.6	57.8	1.7	1.9	9.8
3		28.2	36.1	16.0	76.0	0.5	0.4	7.4
4		14.9	19.0	43.0	51.0	1.0	0.9	4.1
5		18.7	25.6	48.5	43.1	—	2.1	6.1[d]

[a] Reaction conditions: 10 mmol of substrate; 10 mmol of H_2O_2 (31 wt% aqueous solution); Ti-β, 20 wt% with respect to substrate; 5 ml acetonitrile; temperature, 333 K; and reaction time, 6 h.

[b] Corresponding alcohol produced via hydration of olefin and "others" include oligomers.

[c] The reaction was carried out in a closed stainless steel reactor (Parr-type reactor), as the substrate has a low boiling point (boiling point 48°C).

[d] Mixture of allylic oxidation products.

oxidation products. The selectivity of H_2O_2 also decreased considerably as the bulkiness of the substituents attached to the double bond increased. Thus the pinacol formation is controlled by diffusion of reactants rather than by an electronic factor.

Epoxidation of Various Tri- and Tetraalkyl-Substituted Olefins Using Acetonitrile Cosolvent

Table 3 shows the epoxidation of various tri- and tetraalkyl-substituted olefins using acetonitrile as a cosolvent (biphasic system) over the Ti-β/H_2O_2 catalytic system and the activity is considerably lower than that observed under triphase conditions. Due to their hydrophobicity, titanium-silicates will selectively adsorb the organic molecules in triphase operation, leading to a high conversion, in accordance with our earlier report (19). Thus, the least substituted 2-methyl-2-butene (entry 1) shows the highest activity, as in the triphase medium, and the reactivity decreases with increasing number and cross section of the substituents (entries 2 and 3). The *tert*-butyl-substituted (entry 4) and cyclic (entry 5) olefins react very slowly. Furthermore, olefins with four alkyl substitutents (entries 3 and 4) give less epoxide selectivity than the olefins with three alkyl substituents (entries 1, 4, and 5), possibly due to the steric strain of the oxirane ring. The Ti-β catalyst used in the triphase condition was activated at 673 K for 2 h under a flow of air and reused for the oxidation of 2,3-dimethyl-2-butene. The catalyst retained 81% of its original activity after three successive uses. The loss of activity could be partial leaching of titanium from the frameworks either by the action of H_2O_2 or by the side products (20, 21).

Mechanistic Aspects

Mechanistically, the primary epoxide product undergoes nucleophilic ring opening of oxirane to give the final product pinacol over the catalytic Ti-β/H_2O_2/H_2O system. As depicted in Scheme 1, pinacolone can be found in two reaction paths. The primary epoxide can interact with a Brønsted acid site to a *tert*-carbocation (Path A), which undergoes 1,2-migration of the methyl group as carbanion followed by proton elimination to give pinacolone. Alternatively, the pinacol can interact with a Brønsted acid site and undergo dehydration (Path B) to give *tert*-carbocation similar to Path A and the remaining steps would be the same. The amount of pinacolone formed is not increased with an increase in temperature and is always less than 3% (for clarity it is not given in the graph). As the reaction was carried out using excess water, the formation of the carbocation by dehydration (Path B) is not favored. Thus, it is suggested that pinacolone is formed directly from the epoxide rather than from pinacol. Further, 2,3-dimethyl-2-butanol can be formed either via direct olefin hydration or by cation formation from pinacol followed by hydride abstraction from another molecule.

Figure 2 exhibits the existence of appreciable amounts of epoxide in the initial period, which decreased gradually with reaction time. However, the distribution of pinacol and epoxide clearly reveals that pinacol is formed instantaneously as soon as the epoxide is formed, probably because of the strain of the epoxide as well as the high solubility of pinacol in water. Like other oxidation reactions using titanium-silicates, the facile formation of pinacol would be facilitated by successive epoxidation and cleavage by H_2O molecules assisted both by titanium-hydroperoxo complexes formed by the interaction of Ti^{IV} species with H_2O_2 and H_2O, as proposed in the literatures (22, 23), and by Brønsted acid sites.

CONCLUSIONS

The large-pore Ti-β with a three-dimensional channel structure exhibits a high activity and selectivity in the epoxidation and subsequent pinacol formation of tri- and tetraalkyl-substituted olefins using dilute H_2O_2 as oxidant. The reactivity of these olefins increases as the temperature increases from 303 to 333 K. The distribution of products with time reveals that epoxide is the initial reaction product, which is transformed to pinacol by reaction with H_2O. The reactivity of mesoporous porous Ti–MCM-41 is as high as Ti-β, but the medium-pore TS-1, TS-2, and Ti–MCM-22 give a lower conversion than Ti-β or Ti–MCM-41. Acidic titanium-hydroperoxo complexes as well as Brønsted acid sites would promote the nucleophilic ring opening of the oxirane ring by a H_2O molecule to give pinacol in high selectivity. All the titano-silicates produce unwanted acid-catalyzed side products depending upon their Brønsted acid strength. Ti–Al-β produces a large amount of alcohol as hydration product. The activity of these olefins and the H_2O_2 selectivity decrease as the bulkiness or cross section of the substituent increases. Thus, the least substituted 2-methyl-2-butene shows the highest activity whereas 2,4,4-trimethyl-2-pentene shows the lowest activity.

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