



Heterogeneous catalysis

Regioselective epoxidation of different types of double bonds over large-pore titanium silicate Ti-β

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ABSTRACT

Regioselective epoxidation of different types of double bonds located within the cyclic and acyclic parts of bulky olefins has been investigated using large-pore titanium silicate Ti-β in the presence of dilute aqueous H₂O₂ as oxidant under mild liquid-phase conditions. Our experimental results revealed that side-chain vinylic double bonds are selectively epoxidized than those in the cyclohexene-ring. The epoxidation tendency of various bulky olefins with different positional and/or geometric isomers over Ti-β follows the order: terminal -C=C- > ring -C=C- ≈ bicyclic ring -C=C- > allylic C-H bond. Unlike 4-vinyl-1-cyclohexene, epoxidation of an equimolar mixture of cyclohexene and 1-hexene under identical conditions using Ti-β exhibits completely different selectivity and product distributions. Steric factor and accessibility of reactants to active Ti-sites are responsible for the observed regioselectivity of bulky alkenes.

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1. Introduction

Selective catalytic oxidation reactions have been studied extensively for over three decades for the synthesis of value added fine chemicals [1–8]. Epoxidation is an important class of reaction as epoxides are widely utilized as stabilizer, lubricant, additives, surface modifier and so on. The advent of transition metal containing molecular sieves [3–8] has opened new arenas in the selective oxidation chemistry using dilute H₂O₂ as oxidant under liquid-phase conditions. Shape selectivity of molecular sieves or metasilicates often depends on their capability to discriminate molecules on the basis of size with high precision. Those molecules which (both reactant and product) diffuse freely across the channels are found in higher percentage in the product mixture. Furthermore, this kind of shape selectivity has been mostly studied in reversible acid-catalyzed reactions at high-temperature driven by thermodynamic factors as in the case of medium-pore ZSM-5 zeolite. However, the oxidation reactions are normally irreversible and influenced by electronic factor, steric factor and/or restricted transition-state geometry [7]. Thus the reaction rate can be reduced or inhibited altogether if the available space is insufficient to accommodate the steric or geometric demands of the required intermediates or transition states. Furthermore, occasionally the selectivity of a particular product has been increased by some external factors as in the case of hydroxylation of benzene [9] or controlled release of

oxidant as in the case of epoxidation of styrene to styrene oxide using urea/H₂O₂ adduct as an oxidant over medium-pore TS-1 as reported by Laha and Kumar [10].

The selectivity of epoxidation reaction over heterogeneous catalysts is often controlled by hydrophobic microenvironment at the catalyst surface [11]. On the other hand in the homogeneous medium the electronic factor is the main criteria. Clerici and Ingallina [12] have studied the influence of steric factor on the epoxidation of various butene isomers over TS-1 and found that the reactivity was decreased when the number of substituents on the reaction site increases. The steric factor also plays a major role in the chemoselective transformation of functional groups over TS-1 [13]. In the case of chemoselective epoxidation of allyl alcohol, the double bond is selectively epoxidized in the absence of any substituents situated on it; whereas -OH groups of allyl alcohol undergo oxidation when a methyl substituent is located on the double bond. Thus the various factors governing the reactivity of -C=C- is well documented over medium-pore TS-1, whereas large-pore titanosilicates such as Ti-β can show interesting selectivity features depending upon the nature of the double bond. Comparative study on the epoxidation of allyl alcohol, linear olefins, and norbornene has been made over Ti-β and found that epoxidation of allyl alcohol is governed by electronic factor, while norbornene is controlled by steric factor [14]. On the other hand, long chain unsaturated alcohols undergo selective oxidative cyclization to tetrahydrofurans/tetrahydropyrans over TS-1/Ti-β in high yields [15]. We report herein the regioselective epoxidation of different bulky olefins containing two types of double bonds (reaction sites); one is the terminal double bond in the side-chain alkane and in

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the other $-C=C-$ is located in cyclohexene-ring using large-pore Ti- β /H₂O₂ catalytic system. The observed results are corroborated with electronic and steric factors as well as the interaction of different double bonds to active Ti-sites in the channels of titanosilicates. To obtain in-depth knowledge over the selectivity, epoxidation of several linear hexenes, hexadienes, and an equimolar mixture of various terminal alkenes and cyclohexene have also been carried out under similar conditions to understand various factors involved in the regioselective epoxidation of bulky olefins over large-pore Ti- β .

2. Experimental

The synthesis of various titanosilicates has been carried out according to the reported procedures. In a typical synthesis of hydrophobic aluminum-free Ti- β [16] under strongly alkaline medium (pH = 12.6) the following procedure was used: Ti(OBu)₄ (Aldrich) was treated with H₂O₂ at room temperature to form titanoperoxo complex, which was then mixed with 40% aqueous tetraethylammonium hydroxide (TEAOH, Aldrich) while stirring vigorously. Then the required amount of Nipsil VN-3 silica and 3% of dealuminated seed crystals were added followed by additional stirring to get homogeneous paste like gel. The resulting gel (chemical composition: SiO₂:0.025 TiO₂:0.336 H₂O₂:0.55 TEAOH:6.6 H₂O) was transferred into a Teflon-lined autoclave, and the crystallization was carried out at 413 K for 5 days. After crystallization the product was centrifuged, and washed thoroughly with distilled water to remove the organic base. The as-synthesized Ti- β was dried at 373 K and calcined in a controlled flow of O₂ for 12 h at 793 K. The medium-pore TS-1 was synthesized according to the modified procedure by Thangaraj et al. [17]. In a typical synthesis tetraethyl orthosilicate (21 g, TCI) was hydrolyzed by using 33.8 g of tetrapropyl ammonium hydroxide (20% aqueous, Aldrich) for 3 h under vigorous stirring. Then 1.15 g tetrabutyl orthotitanate in 5 g of anhydrous isopropyl alcohol was added dropwise while stirring. After 1 h of continuous stirring, 27 g water was added into the resulting clear homogeneous liquid, and the crystallization was carried out at 443 K for 24 h under agitation. After crystallization, the solid product was washed, dried, and calcined at 823 K for 12 h. In the case of TS-2 [18], the synthesis procedure is similar to that of TS-1 except that tetrabutylammonium hydroxide was used as organic base, and the crystallization was carried out under static conditions.

The synthesis of microporous Ti-B-MCM-22 [19] was carried out as follows: an aqueous solution prepared by dissolving piperidine in deionized water was divided into two equal parts. Required amount of tetrabutyl orthotitanate or boric acid was added to each piperidine solution under vigorous stirring. Silica was also divided into two equal parts and added gradually to the solutions containing Ti and B. The gels were then mixed together and stirred for 2 h to obtain a gel with the following molar composition of SiO₂:0.02 TiO₂:0.67 B₂O₃:1.4 piperidine:19 H₂O. The crystallization was carried out by keeping the gels in an air-tight autoclave through progressive heating at 403, 423 and 443 K for 1, 1 and 5 days, respectively. After the crystallization, the solid was dried and the extra framework B- and Ti-species were removed by treatment with 2 M HNO₃ at 373 K for 20 h. The samples were calcined at 803 K to remove the remaining organic species. The mesoporous Ti-MCM-41 was synthesized using dodecyltrimethyl ammonium chloride (TCl) and tetramethyl ammonium hydroxide (20% aqueous) according to the reported procedure [20].

The catalytic reactions were carried out in a 25 mL round bottom glass reactor fitted with a water condenser through which ice-cold water was circulated. In a typical reaction 5 mmol of substrate, 5 mmol of H₂O₂ (31 wt% aqueous), 20 wt% of Ti- β (Si/Ti = 43) with respect to substrate and 5 mL of methanol were mixed together

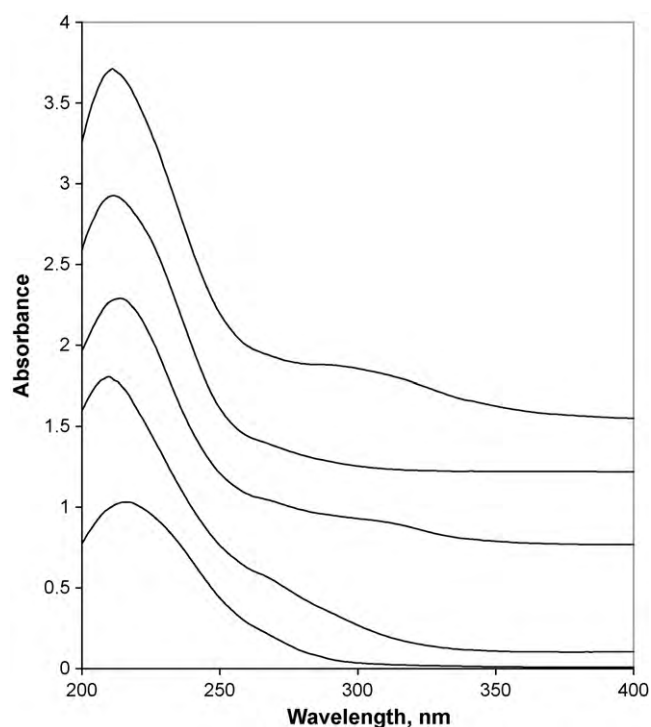


Fig. 1. UV-vis spectra of different titanosilicates; (bottom to top) TS-1, TS-2, Ti-B-MCM-22, Ti- β and Ti-MCM-41, respectively.

and the contents were vigorously stirred using a magnetic stirrer. Bromobenzene was used as an internal standard for the estimation of various products. Progress of the reaction was monitored by analyzing the reaction mixtures at various time intervals with a capillary gas chromatograph (Shimadzu 14A, OV-1 columns with flame ionization detectors). The various authentic epoxy products were purchased commercially and also converted into diol products (to confirm the diol products formed in the reaction mixture) using H-mordenite catalyst. Furthermore, GCMS splitting pattern was also employed to identify the unknown products.

3. Results and discussion

3.1. Characterization of the catalysts

All the above-synthesized titanosilicates were characterized using XRD, FTIR and UV-vis spectroscopy, and scanning electron microscopy. The powder X-ray diffractograms of various titanosilicates and the corresponding scanning electron microscope images reveal that the samples are phase pure and completely free from amorphous materials. Furthermore, FTIR spectra of these samples show characteristic absorption band at 960 cm⁻¹ suggesting the presence of titanium in the framework position. Fig. 1 shows the UV-vis spectra of various titanium silicates. The presence of strong band at 220 nm and the absence of any band either at 260 or 300 nm indicate the absence of octahedral TiO₂ cluster as impurities and thus titanium sites exist mainly in the tetrahedral positions [21] in the framework of Ti- β .

3.2. Effect of reaction temperature and time

The regioselective epoxidation of 4-vinyl-1-cyclohexene with double bonds both at side-chain and cyclohexene-ring has been investigated systematically using Ti- β by scrutinizing the reactivity at different temperature and time. Fig. 2 illustrates the progress in olefin conversion at different time intervals. Separate experi-

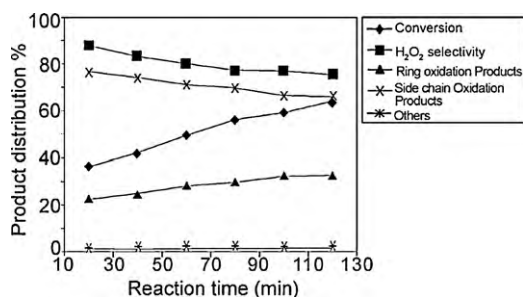


Fig. 2. Effect of reaction time on the activity and product distributions in the partial oxidation of 4-vinyl-1-cyclohexene over Ti-β.

mental runs were carried out under identical conditions for each point of the graph to get better mass balance. The various products formed on epoxidation of 4-vinyl-1-cyclohexene are illustrated in Scheme 1. The epoxidation of side-chain vinylic $-C=C-$ mainly produced the solvolyzed glycol-monomethyl ether in addition to small amount of the corresponding epoxide, aldehyde, and ketone when methanol was used as solvent. For convenience the above mixture of products is called “side-chain epoxidized products” in the subsequent discussion. In addition, the $-C=C-$ located inside the cyclohexene-ring produces epoxide as the major products; in particular diepoxide, a product with oxirane moieties situated both at the vinylic-carbons and cyclohexene-ring is found to be the predominant product with traces of cyclohexene-monoepoxide; No corresponding polyol/polymethoxylated products were detected and combination of these products are called “ring epoxidation products”. It is seen from Fig. 2 that 4-vinyl-1-cyclohexene conversion increases with time as expected. Further, the product distribution pattern suggests that, selectivity for the side-chain epoxidized products is considerably higher than the cyclohexene-ring derivatives. At the initial stage of reaction the selectivity for the “side-chain epoxidation” is considerably high, which decreased gradually due to successive reaction of primary products to produce diepoxide or ring epoxidation products. The percentage of these secondary products increased as the reaction is progressed. The other products in Fig. 2 refer to the allylic oxidation of C-H bond at the allylic position of the cyclohexene nucleus. After completion of reaction in about 2 h, the conversion of H₂O₂ reached 92% with selectivity of 78.0% for the epoxidation.

Fig. 3 exhibits the product distribution in the temperature range of 303–338 K using Ti-β/H₂O₂ catalytic system in methanol solvent. At low temperature, Ti-β shows less activity particularly at 303 and 313 K but the activity increased significantly after 323 K. Furthermore at temperatures below 323 K, the reaction of vinylic $-C=C-$ bond with active sites occurs smoothly than the cyclohexene-ring

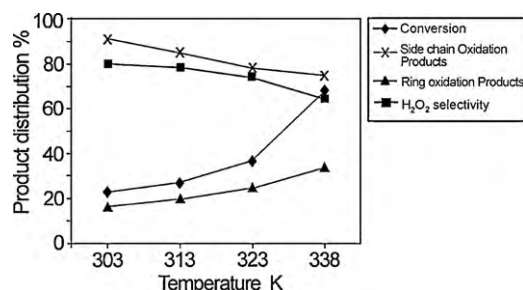
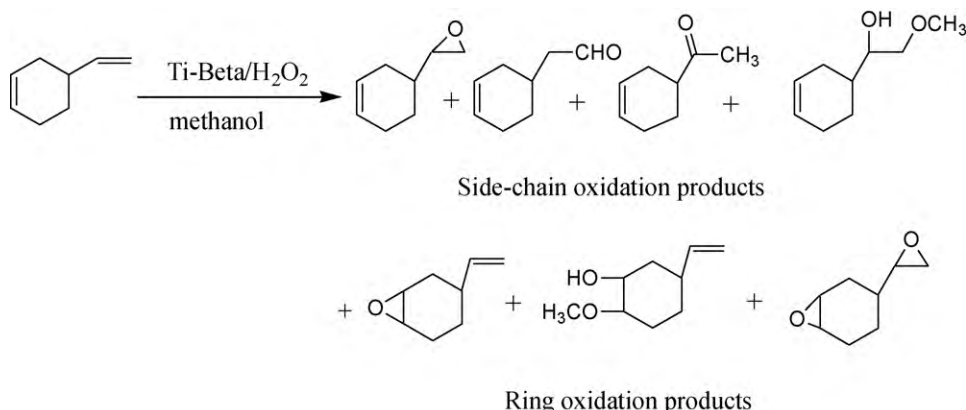


Fig. 3. Effect of temperature on the activity and product selectivity in the partial oxidation of 4-vinyl-1-cyclohexene over Ti-β.

leading to high selectivity for the side-chain $-C=C-$ epoxidation products. Nevertheless, as the temperature increases from 303 to 338 K, not only the activity of the Ti-β improves but it also increasingly favors cyclohexene epoxidation probably due to easy access of cyclic double bond. The high temperature also accelerates the rate of consecutive reaction such as the transformation of monoepoxide into diepoxide, which is the major product in “ring epoxidation products”. Thus the selectivity for the bulky cyclohexene-ring epoxidation increased at the expense of side-chain vinylic epoxy products. The H₂O₂ selectivity decreased as the temperature increased as expected.

3.3. Effect of various titanium silicates

The epoxidation reaction has also been screened over various titanasilicates such as TS-1, TS-2, Ti-B-MCM-22, Ti-β, and Ti-MCM-41 with different pore openings under identical reaction conditions and obtained results are summarized in Table 1. Among the various catalysts investigated, Ti-β (entry 1) with large-pores coupled with three-dimensional pore connectivity shows the best activity for the epoxidation of 4-vinyl-1-cyclohexene. The side-chain vinylic $-C=C-$ undergoes facile epoxidation (66.7%) than the cyclohexene-ring (32.2%). Thus the epoxidation of vinylic double bond proceeds smoothly to corresponding epoxy products than the cyclohexene-ring. Unlike Ti-β, medium-pore titanasilicates such as TS-1 (ZSM-5 structure, pore width 5.6 Å × 5.3 Å) and TS-2 (ZSM-11 structure, pore width 5.4 Å × 5.3 Å) show less activity for the oxidation of 4-vinyl-1-cyclohexene probably due to internal diffusion limitation of bulky reactant and/or products in the channels of these zeolites [22,23]. Nevertheless the epoxidation of side-chain $-C=C-$ takes place smoothly than that located at the six-membered cyclic ring which is consistent with the literature reports that the TS-1 is highly suitable for the epoxidation of linear alkenes compared to cyclohexene. But in the present study of epoxida-



Scheme 1. Product distribution for the liquid-phase oxidation of 4-vinyl-1-cyclohexene over Ti-β.

Table 1
Influence of various titanium silicates for the epoxidation of 4-vinyl-1-cyclohexene.^a

Sr. no.	Catalyst	Particle size ^c , μm	Conv. mole, %	H ₂ O ₂ sel., %	Selectivity of products, %			Ratio ^d
					Side-chain oxidized products	Ring oxidized products	Others	
1	Ti-β (43) ^b	1.0	64	75	67	32	1.0	0.5
2	TS-1 (33) ^b	0.1–0.2	18	88	96	4	–	0.03
3	TS-2 (46) ^b	2–3	16	82	97	3	–	0.03
4	Ti-B-MCM-22 (55) ^b	0.2–0.5	37	92	89	11	–	0.12
5	Ti-MCM-41 (51) ^b	0.2–0.5	12	61	87	13	–	0.13
6	Ti-β (43) ^b	1.0	21 ^e	90	79	21	–	0.26
7	Ti-MCM-41 (51) ^b	0.2–0.5	19 ^f	46	85	14	–	0.16

^a Reaction conditions: 5 mmol of 4-vinyl-1-cyclohexene; 5 mmol H₂O₂ (31 wt% aqueous solution); 5 mL methanol; catalyst, 20 wt% with respect to substrate; temperature, 338 K; and reaction time 2 h.

^b The figures in the parentheses refers to Si/Ti ratio.

^c Particle size observed from scanning electron microscope.

^d Ratio of cyclohexene to vinylic side-chain –C=C– oxidation products.

^e Reaction was performed for 10 min to reduce the conversion.


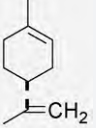



^f Reaction was performed for 5 h to increase the conversion.

tion of 4-vinyl-1-cyclohexene, it is highly likely that the double bond in the side-chain or tail can interact with the Ti-sites through the medium-pores to provide “side-chain epoxidized products”. Entry 4 exhibits the activity of Ti-B-MCM-22, which is considerably higher than TS-1 or TS-2; the increased performance may be due to the presence of Ti-species in the 10-ring channels, supercages, and the exterior pockets, which permit the easy access of the bulky olefins to the active sites. However, selectivity for the “side-chain epoxidized products” is invariably high (89%) irrespective of the conversion level over these titanasilicates.

Ti-MCM-41 (entry 5), the titanium analogue of mesoporous MCM-41 exhibits still less activity (12.1%) than the other titanasilicates in spite of having less diffusion limitation or steric hindrance. It has been reported in the literature that [24] the catalytic per-

formance of Ti-MCM-41 in the epoxidation of linear olefins like 1-hexene was found to be less compared to cyclic or bulky olefins. Furthermore, intrinsic activity of Ti-MCM-41 could be less because the mesopores contain a large number of Si–OH groups, which strongly adsorbs methanol and H₂O₂ under the reaction conditions and the apolar substrate (4-vinyl-1-cyclohexene) is adsorbed weakly, thus hindering the intrinsic activity of Ti-MCM-41. Moreover the selectivity for “side-chain epoxidized products” was found to be 87%. Thus the catalytic performance of Ti-MCM-41 was also found to be similar to that of microporous titanium counterparts although former has mesopore architecture. Thus the activity of Ti-β is different in the sense that it resembles to that of medium-pore TS-1, TS-2 and Ti-B-MCM-22 by forming more side-chain vinylic epoxidation products contrary to the expectation. In addition,

Table 2
Epoxidation of various cyclic olefins over Ti-β/H₂O₂ system.^a

Sr. No	Substrate	Conv. mole, %	H ₂ O ₂ sel., %	Product distribution			Ratio ^d
				Side-chain oxidation products	Ring oxidation products	Others	
1		32.7 ^b	58.5	64.4	33.7	1.8	0.52
		64.1 ^c	75.3	66.1	32.5	1.4	0.51
2		28.5 ^b	61.0	60.2	36.3	3.4	0.6
		73.7 ^c	80.4	58.5	37.3	4.1	0.37
3		23.9 ^b	81.5	95.0	5.0	–	0.05
		55.6 ^c	86.6	71.5	26.6	1.9	0.37
4		26.9 ^b	69.0	43.0	52.6	4.3	1.22
		71.2 ^c	90.5	54.6 ^e	40.3	4.0	0.73
5		25.8 ^b	38.0	–	67 ^f , 15 ^g , 18 ^h	–	–
		34.4 ^c	49.0	–	65 ^f , 21 ^g , 14 ^h	–	–

^a Reaction conditions: 5 mmol of substrate; 5 mmol of H₂O₂ (31 wt% aqueous solution); catalyst, 20 wt% with respect to substrate; 5 mL solvent; temperature 338 K; and reaction time, 2 h.

^b Acetonitrile was used as solvent.

^c Methanol was used as solvent.

^d Ratio of ring double bond to side-chain epoxidation products.


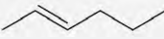
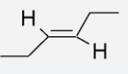
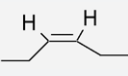
^e Epoxy products of exo double bond.

^f Epoxidation product.

^g Allylic products.

^h Unknown products, possibly aromatic oxidation products.

Table 3
Epoxidation of open-chain hexene isomers over Ti-β/H₂O₂.^a

Entry	Substrate	Conv. mole, %	H ₂ O ₂ sel., %	Product distribution, %		
				Epoxy products	Allylic oxidation products	Others
1		45.3	68.6	92.2	3.8	4.0
2		52.0	78.4	92.7 (80.5% epoxide)	7.3	–
3		52.2	83.4	85.3	9.7	5.0
4		61.0	87.6	89.0	4.6	6.4

^a Reaction conditions: 5 mmol of substrate; 5 mmol of H₂O₂ (31 wt% aqueous solution); catalyst, 20 wt% with respect to substrate; 5 mL methanol; temperature 338 K; and reaction time, 2 h. “others” refer to a low boiling compound.

the ratio of “ring epoxidation products” to “side-chain epoxidized products” is always much higher for large-pore Ti-β than either Ti-MCM-41 or other medium-pore titanasilicates. We have also attempted to compare the above ratios at similar conversion levels by increasing the reaction time for the reaction over Ti-MCM-41 (entry 7, conversion = 19.1%), and decreasing that of Ti-β (entry 6, conversion = 20.7%), but the observed product distribution is again quite high for “side-chain epoxidized products”. Therefore the reactivity and product distribution of these two types of double bonds in 4-vinyl-1-cyclohexene reveal that: (i) the medium-pore titanasilicates TS-1, TS-2, and Ti-B-MCM-22 exhibit high selectivity for vinylic/terminal –C=C– epoxidation (ii) large-pore Ti-β and mesoporous Ti-MCM-41 also show preferential epoxidation of vinylic double bonds and these results contrast with previous reports that Ti-β smoothly epoxidize the cyclohexene-ring. Driven by the curiosity from the above results, the regioselective epoxidation was further studied thoroughly with various bulky alkenes containing two types of double bonds using Ti-β as the catalyst as it displays the best activity.

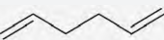


3.4. Epoxidation of different bulky olefins with two types of double bonds over Ti-β

Table 2 exhibits the reactivity and product selectivities toward different bulky olefins containing two types of double bonds investigated using Ti-β/H₂O₂ catalytic system. In addition to methanol, we have also employed acetonitrile solvent (entry 1) to observe any pattern change in the product selectivity. It is relevant to mention that the experiment involving acetonitrile solely produced epoxide, aldehyde (after rearrangement), and diol products for 4-vinyl-

1-cyclohexene; whereas glycol-monomethyl ether was obtained predominantly due to further rearrangement of the products in the presence of methanol solvent (entry 1). In addition the reactivity of 4-vinyl-1-cyclohexene in acetonitrile is decreased almost by one half compared to that in methanol but the selectivity for “side-chain epoxidized products” is dominated as observed in the case of methanol. These two experiments by using different solvents obviously indicate that the solvents play very little role in determining the selectivity and/or reactivity of different –C=C– bonds. However, one would expect that the epoxidation of the double bond in the cyclic ring should be faster than the terminal double bond and this is indeed the case for the homogeneously catalyzed epoxidation reaction [25]. Thus the above results indicate that besides electronic factor, possibly the steric factor also plays dominant role in the epoxidation.

In the case of limonene (entry 2) both terminal and cyclic –C=C– has a methyl group in its vicinity and therefore terminal –C=C– is again preferentially epoxidized over the cyclic system immaterial of the solvents used. The substrate 4-vinyl-1-norbornene with bicyclic ring skeleton (entry 3) shows very good regioselectivity towards side-chain epoxidation with subsequent isomerization to the corresponding aldehyde in 95% yield in acetonitrile and negligible amount of ring epoxidation; whereas for the same substrate methanol medium produced considerable amount of “ring epoxidation products” (26.6%) at the expense of “side-chain epoxidized products” (71.5%). The reactivity of 4-ethylidene-1-norbornene (entry 4), a compound with exo double bond with a methyl substituent shows increased reactivity of –C=C– inside the bicyclic ring system. The different reactivity pattern of 4-ethylidene-1-norbornene may be due to conformational and steric hindrance of

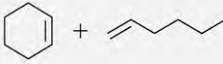
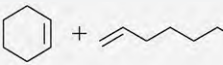
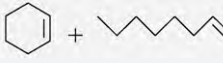
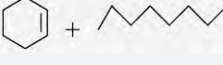
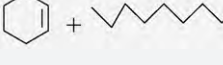
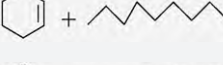

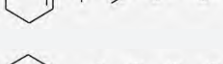
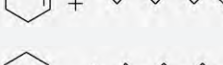
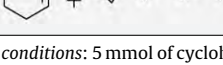
Table 4
Epoxidation of hexadiene isomers over Ti-β/H₂O₂.^a

Substrate	Conv. mole, %	H ₂ O ₂ sel., %	Product distribution, %				
			Terminal epoxy products	Internal epoxy products	Diepoxy products	Allylic oxidation	2,4-Hexadiene ^b
	48.6	52.9	32.8	–	29.6	3.8	33.8
Trans- 	55.0	49.0	5.7	28.9	24.9	4.8	36.5
Trans- 	46.1	51.0	15.4	37.4	12.5	2.2	32.5

^a Reaction conditions: 5 mmol of substrate; 5 mmol of H₂O₂ (31 wt% aqueous solution); catalyst, 20 wt% with respect to substrate; 5 mL methanol; temperature 338 K; and reaction time, 2 h.

^b 2,4-Hexadiene is readily formed by isomerization since the conjugated internal diene is highly stable.

Table 5
Epoxidation of equimolar mixture of cyclohexene and various terminal olefins over Ti-β/H₂O₂.^a

Entry	Substrates	Cyclohexene				Terminal alkenes			H ₂ O ₂ sel., %
		Conv., mole, %	Epoxide, %	Diol, %	Others ^d , %	Conv., mole, %	Epoxide, %	Diol, %	
1 ^b		23.8	42.0	56.6	1.4	14.1	83.3	16.7	83.0
2 ^b		19.5	42.6	55.6	1.8	13.3	91.3	8.6	79.0
3 ^b		19.9	40.0	57.5	2.5	11.5	90.5	9.5	80.8
4 ^b		19.6	29.3	69.3	1.4	10.9	91.0	9.0	82.5
5 ^b		20.5	22.8	75.8	1.4	11.0	91.8	8.2	75.2
6 ^b		19.4	27.6	71.5	0.9	10.3	91.0	9.0	76.5
7 ^b		21.0	27.5	72.5	-	10.6	92.1	7.9	76.1
8 ^c		12.4	5.2	92.4	2.2	2.1	68.8	31.2	45.9
9 ^c		11.9	7.1	89.3	3.6	1.9	72.0	28.0	47.5
10 ^c		12.5	7.2	90.8	2.0	1.1	71.0	29.0	44.0

^a Reaction conditions: 5 mmol of cyclohexene and 5 mmol of terminal alkene; 10 mmol of H₂O₂ (31 wt% aqueous solution); catalyst, 20 wt% with respect to substrate; 10 ml acetonitrile; temperature 338 K; and reaction time, 2 h.

^b Ti-β.

^c Ti-MCM-41.

^d Others indicates allylic oxidation products.

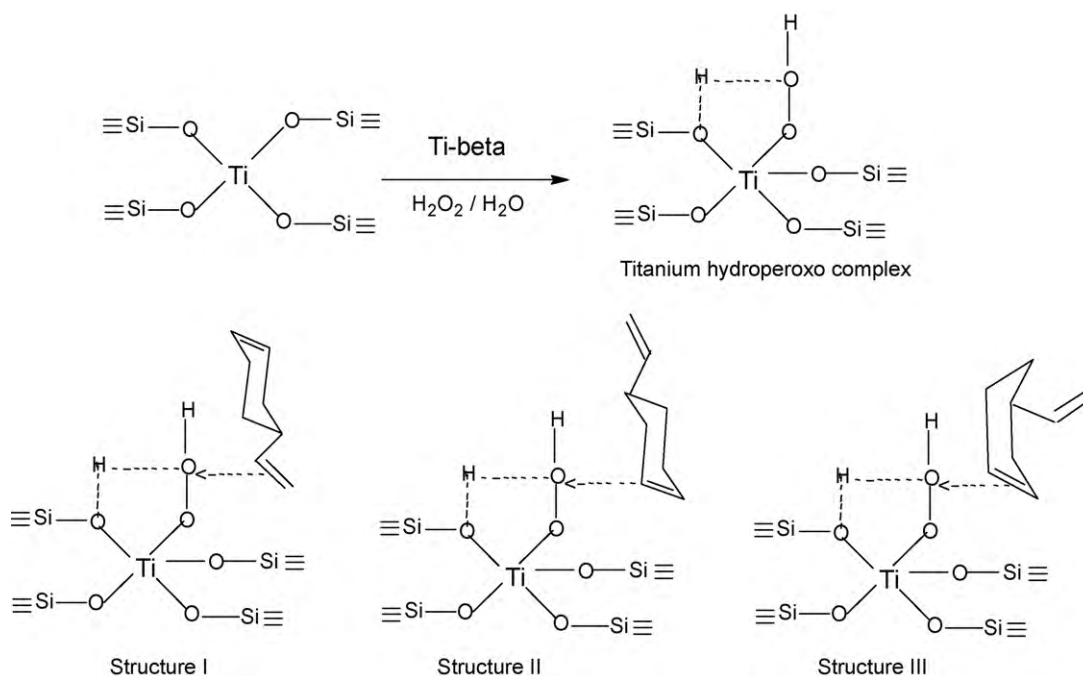
exo double bonds toward the accessibility to active Ti-sites. In addition, the exo -C=C- at the bicyclic ring is flanked by three methyl substituents, whereas that in the bicyclic ring is strained by two methyl substituents. As a result the -C=C- in the ring is relatively less hindered and reacts faster by interacting with active sites in the porous matrix. The substrate 1-phenylcyclohexene (Table 2, entry 5) illustrates the oxidizing ability of Ti-β towards -C=C- bond versus aromatic C-H bond. Our experimental results suggest that the oxidation predominantly takes place at the -C=C- bond followed by allylic position, whereas the aromatic C-H bond is least affected. The observed H₂O₂ selectivity is slightly higher in the case of methanol due to increased reactivity than acetonitrile.

The above investigation over various alkenes with different types of -C=C- bonds clearly reveals that Ti-β exerts less diffusion limitation as it smoothly epoxidize both side-chain vinylic as well as cyclic ring system. However, the observed product selectivity appears to be influenced mostly by both steric crowding around the -C=C- bond, and conformational flexibility of these substrates near the active Ti-sites. Thus, when a molecule has more than one double bonds (reaction sites) in different position, the more accessible one reacts readily than the one, which is not accessible. The accessibility of the reaction sites is ultimately governed by the steric hindrance, geometry and/or conformation of the interacting or reacting molecules with the active Ti-species under the experimental conditions. The observed results over these bulky olefins

suggest that, the vinylic -C=C- bonds are easily accessible than the one at cyclic ring unless the terminal -C=C- is highly crowded by many substituents as in the case of 4-ethylidene norbornene (entry 4) with exo double bond. Thus the oxidation of different double bonds, allylic -C-H, and aromatic -C-H within the same molecule follows the order: terminal -C=C- > cyclic ring -C=C- ≅ bicyclic -C=C- > allylic C-H > aromatic C-H.

3.5. Comparison of reactivity of various hexene isomers

To gain further insight in the reactivity behavior of side-chain terminal double bonds, a series of experiments were carried out with various hexene and hexadiene isomers (linear olefins) over Ti-β under similar experimental conditions and the results are summarized in Tables 3 and 4. The conversion as well as H₂O₂ selectivity of 1-hexene (terminal alkene, Table 3, entry 1) is lower than that of *trans*-2-hexene (an internal alkene, entry 2) consistent with the earlier report [14], and the increased activity of 2-hexene is attributed to the electron releasing inductive effect of methyl substituents. Entries 3 and 4 (Table 3) exhibit the reaction of *trans*- and *cis*-3-hexene (geometrical isomers); the *trans*-3-hexene is less reactive than the *cis*-3-hexene suggesting that the reaction site is less hindered in the case of later than the former leading to higher conversion. Thus though the Ti-β is comprised of large-pore structure



Scheme 2. Transition-state intermediates at the Ti- β surface during the liquid-phase oxidation of 4-vinyl-1-cyclohexene over Ti- β with dilute aqueous H_2O_2 .

with a free flow of molecules in all the direction along the channels, the geometry and conformational flexibility of a molecule vis-à-vis accessibility to the active sites also determines the reactivity.

Furthermore, linear 1,5-hexadiene (entry 1, Table 4) with two $-\text{C}=\text{C}-$ bonds located at the terminal positions shows less reactivity (48.6%) than other dienes with both terminal as well as internal $-\text{C}=\text{C}-$ bonds. The higher reactivity of 1,4-hexadiene (55.1%) over 1,5-hexadiene could be due to the favorable electronic factor (alkyl substitution) in the former. But the reactivity of conjugated 1,3-hexadiene (entry 3, Table 4) was lower than 1,4-hexadiene, possibly increased stability due to conjugation may resist the oxidation. Thus the epoxidation of internal $-\text{C}=\text{C}-$ bond dominates over the terminal counterparts for 1,4- and 1,3-hexadiene isomers. It is important to note that all three hexadiene isomers undergo isomerization to give the most stable conjugated 2,4-hexadiene as the major side product. This could be facilitated either by acidic titaniumhydroperoxo complex or weak Brønsted acidity of Ti- β itself. Thus the reactivity of side-chain and/or internal $-\text{C}=\text{C}-$ is governed mainly by the electronic factor in the case of hexene and hexadiene isomers except 3-hexene geometrical isomers where steric factor plays a dominant role. The above results over linear olefins clearly demonstrate that the reactivity of terminal double bond is always lower than the internal double bonds confirming the earlier reports. To prove the reactivity of 4-vinyl-1-cyclohexene and similar substrates without any ambiguity, a series of experiments were performed by externally mixing the individual compounds of cyclohexene (ring $-\text{C}=\text{C}-$) and different terminal alkenes (terminal $-\text{C}=\text{C}-$) in an equimolar amounts.

3.6. Epoxidation of equimolar mixture of cyclohexene and different terminal alkenes

The experiments were carried out using Ti- β /H₂O₂/acetonitrile catalytic system under similar experimental conditions and the reactivity along with product distribution are given in Table 5. Entries 1–7 (Table 5) show the epoxidation of an equimolar mixture of various linear terminal alkenes of C₆[≡] to C₁₂[≡] with cyclohexene. Among the bulky cyclohexene and linear terminal alkenes, the for-

mer showed more conversion than the later in accordance with the literature reports [22]. As the length of terminal olefins increases gradually from C₆[≡] to C₁₂[≡], the conversion of cyclohexene is not decreased appreciably though it fluctuated within a range. This result suggests that large-pore Ti- β exhibits very little diffusion limitation for the epoxidation of a mixture of cyclohexene and *n*-hexene unlike medium-pore TS-1, where diffusion play a major role to provide more *n*-hexene epoxidation [26,27]. Furthermore, the epoxidation of cyclohexene mainly produced the corresponding cyclohexane-1,2-diol as the major product and the percentage of diol product also increases with chain length of the linear terminal alkenes, probably due to the increased molecular traffic along the channels which makes the epoxides prone to hydrolysis before it is dragged away to the bulk reaction medium.

The conversion of various linear terminal alkenes are invariably lower than cyclohexene and it decreased slightly as the chain length increases from C₆[≡] to C₁₂[≡]; probably steric effect plays a role as the hydrophobic alkyl chain length increases. These terminal olefins produced epoxides as the major product with a small amount of the corresponding diol. Entries 8–10 show the reactivity over Ti-MCM-41 and also exhibits increased epoxidation towards cyclohexene-ring rather than terminal olefins but the observed activity was found to be lower comparable to Ti- β . The difference in activity between Ti- β and Ti-MCM-41 is presumably due to amorphous pore wall with high hydrophilic interior and/or inaccessibility of titanium active sites located inside the silica walls of Ti-MCM-41 as reported by Oldroyd et al. [28]. Thus the above experiments clearly reveal that the nature of the active sites of these two titanosilicates differ intrinsically; presumably the bond length and/or bond angles of the coordinated Ti atom may play a role in the formation of titaniumhydroperoxo complex with H₂O₂, and subsequent release of oxygen atom to the organic substrate during the reaction. Thus the above experiments using an equimolar mixture of cyclohexene and terminal alkenes confirm the earlier reports that Ti- β is more active towards bulky cyclohexene than the terminal alkenes. However, the selectivity and product distribution is altered for bulky alkenes with both terminal and cyclic double bonds as observed in the present study. The catalyst Ti- β retains 86% of original activity after five successive reuses after activation

at 573 K for 5 h for the epoxidation of 4-vinyl-1-cyclohexene. The loss of activity may be due to the partial removal of framework titanium either by the action of H_2O_2 or the bulky reaction products such as diol and glycol-monomethyl ethers as reported by Davis et al. [29].

3.7. Mechanistic aspects

The epoxidation of 4-vinyl-1-cyclohexene over Ti- β / H_2O_2 catalyst system proceeds smoothly as shown in Fig. 2. The experimental results reveal that primary epoxy products both cyclic and acyclic-derivatives undergo consecutive secondary reactions assisted by either weak Brønsted acid sites of Ti- β or acidic titanium hydroperoxo complex [30,31]. Thus, the acyclic or terminal epoxides produce aldehyde and ketone by isomerization; whereas diol and glycol-monomethyl ethers are formed by the nucleophilic ring opening reaction with H_2O and CH_3OH molecules, respectively. In addition, terminal epoxide also undergoes further epoxidation of double bond in the cyclohexene-ring to produce diepoxide, which is the major product among the “Ring epoxidation products”. From the observed product distribution it is obvious that the stability of diepoxide is quite higher compared to monoepoxide as seen from negligible amount of polyol or polymethoxylated product formation.

The observed reactivity of compounds with cyclic- and acyclic double bonds over Ti- β is however in contrast with the literature, i.e. $-\text{C}=\text{C}-$ in the cyclic ring should be more reactive than the terminal $-\text{C}=\text{C}-$ bond. Furthermore the epoxidation of other similar substrates also showed high reactivity towards terminal double bonds. The observed reactivity can be explained by considering the formation of possible Ti-species or intermediate that leads to epoxidation and the kind of interaction between such active intermediate with 4-vinyl-1-cyclohexene is illustrated in Scheme 2. The interaction of H_2O_2 with Ti-site produces five coordinated species (titanium hydroperoxo complex) [30–32], which could be stabilized due to the formation of 5-membered ring. This not only makes the hydroperoxo complex Brønsted acidic but also the peroxyoxygen becomes more electron deficient. Now the interaction of these activated intermediates in the channels and pores of Ti- β with 4-vinyl-1-cyclohexene or other substrates play a crucial role in determining the reactivity of a particular double bond. Thus, the interaction of terminal $-\text{C}=\text{C}-$ with active Ti-intermediate (Structure I, Scheme 2) undergoes less strain as it contains no substituents on the double bond. However, in the case of cyclohexene-ring of 4-vinyl-1-cyclohexene, which exist in two different conformational structures i.e. chair and boat (boat form of cyclohexene is less stable than the chair form) forms makes the interaction more difficult (Structure II and III, Scheme 2). The observed low reactivity vis-à-vis selectivity for cyclic ring oxidation at lower temperature (Fig. 3) may be the consequence of conformational as well as steric resistance towards the accessibility at the active Ti-sites. Thus, the observed product distribution can be explained by considering the interaction of a molecule as a whole entity instead as ‘terminal’ or ‘cyclic’ double bonds. Therefore, the epoxidation of terminal $-\text{C}=\text{C}-$ occurs prominently unless it is highly strained by many substituents as in the case of 4-ethylidene-1-norbornene with exo double bond. The same explanation can also hold good for geometrical isomers, where the interaction of *cis*-isomer is more effective than the *trans*-isomer.

4. Conclusions

Our experimental results suggested that large-pore titanium silicate Ti- β exhibited high catalytic activity in the epoxidation of cyclic and acyclic double bonds. The reactivity of different bulky olefins has been governed by steric hindrance and/or conformational flexibility near the active Ti-sites. Among the various bulky olefins investigated using Ti- β catalyst, the epoxidation efficiency follows the order: terminal $-\text{C}=\text{C}-$ > cyclic ring $-\text{C}=\text{C}-$ \cong bicyclic $-\text{C}=\text{C}-$ > allylic C–H. Epoxidation of various hexene and hexadiene isomers indicated that internal alkenes smoothly epoxidize than the terminal alkenes. The mesoporous Ti-MCM-41 showed similar selectivity as that of Ti- β but with lower activity in spite of its negligible diffusion limitation. The difference in the activity between Ti- β and Ti-MCM-41 is attributed to the intrinsic nature of local Ti-site and crystalline framework of Ti- β . Thus the present investigation, for olefins containing more than one double bonds (reaction sites) at different position suggested that the reactivity is ultimately governed by the steric hindrance, geometry and/or conformational flexibility of the interacting molecules at the active Ti-active sites.

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