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Epoxidation of cyclic alkenes with hydrogen peroxide and *tert*-butyl hydroperoxide on Na-containing Tiβ zeolites

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Abstract

The liquid-phase epoxidation of a series of cyclic alkenes with H_2O_2 and TBHP over Na–Tiβ zeolites without undergoing further acid-treatment has been carefully investigated. Many factors such as the time, the conversion, the solvent, the Si/Na ratio, the Si/Ti ratio and the Ti/Na ratio, have been found to take effects on the conversion of cyclohexene and H_2O_2 as well as the selectivity to epoxide. Lower conversion (about 6.2 mol%) of cyclohexene has shown an improvement for the selectivity to epoxide (about 90%). The solvent having bigger dielectric constant is very helpful to enhance the reactivity of substrate, particularly MeCN is an optimal choice for improving the selectivity to epoxide (up to 59%). The reactivity of cyclic alkenes decreases with increasing carbon number from C6 to C12, the selectivity to corresponding cyclic epoxides is C12 $\approx$ C8 (100%) $>$ C7 (71%) $>$ C5 (20%) $>$ C6 (1.2%), where the exception of C5 is related to its low dissolubility and steric conformations of reactant and products molecules. Linear alkene shows the higher reactivity and the lower selectivity to epoxide than cyclic alkene with the same carbon number. TBHP as the oxidant significantly retards the reactivity of C6, C7 and C12, and shows more beneficial to the selective production of epoxide than H_2O_2. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Na–Tiβ; Liquid-phase oxidation of cyclic alkenes; Epoxidation; Titanium zeolites; Hydrogen peroxide; TBHP

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1. Introduction

The catalytic properties of TS-1 and TS-2 appeared to be unique. In oxidation reactions using H_2O_2 as the oxidant, many organic compounds could be obtained with high yields, and almost all the oxygen available from H_2O_2 was used to produce the desired compounds, with only slight decomposition to give H_2O and O_2 [1].

Owing to the dimension of the channels of these pentasil zeolites (≈5.5 Å), they have shown severe restrictions to oxidize large organic reactants with H_2O_2 as an oxidant [2,3]. This led to the synthesis of large pore materials such as Tiβ [4], Ti-MCM-41 [5] and Ti-MCM-48 [6]. Zeolite Tiβ is the only Ti-containing zeolite synthesized up to now possessing a three-dimensional pore system of 12-membered ring channels. The pore diameter of Tiβ is ca. 7 Å, larger than that of TS-1 and TS-2. Tiβ was shown to be more active than TS-1 for the oxidation of bulkier substrates, such as cyclic and branched molecules [7].

Though alkali metals do not affect the synthesis of most zeolites, and in many cases are even required, they do influence the synthesis of titanium silicates [8–12]. Attempts to perform the synthesis of TS-1 in the presence of alkali metals either failed or produced

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materials with inferior catalytic properties [13]. The samples of TS-1 prepared in the presence of Li, Na and K in the precursor gel produced materials that had considerable amounts of extra framework TiO_x, poor catalytic properties, and gave a high rate of H_2O_2 decomposition. Clerici and Ingallina [14] reported, however, that small amounts of basic compounds could improve the selectivity by decreasing the acid strength inside the pore system of TS-1. The effect of the alkali metal exchange (Li, Na, K, Ba and Mg) on the selectivity and activity of the catalyst TS-1 was also investigated by Sheldon et al. [15], who concluded that in the case of TS-1, it was possible to enhance the selectivity using the pretreatment with base without decreasing the activity. Khouw and Davis [16] further claimed that when the amount of Na in the synthesis gel was very low ($Si/Na \geq 100$), the TS-1 obtained contained some extra framework TiO_x, but could be reactivated by treatment with H_2SO_4 to give a catalytic activity comparable to that of TS-1 synthesized in the absence of Na and having equal Ti content.

The synthesis of Tiβ zeolites has been carried out by direct hydrothermal synthesis and by secondary synthesis, whereas in all hydrothermal syntheses, the use of alkali metal ions was completely avoided. In contrast with TS-1, the crystallization of Tiβ requires some Al as a framework constituent when tetraethyl ammonium ion (TEA) is used as the structure directing agent [4]. The Al-free Tiβ crystallizes merely under very specific conditions, such as the synthesis in fluoride medium, or using a special template or using the seed crystals [17–19]. This drawback imparts strong protonic acidity to the solid, with the consequence that acid-catalyzed secondary reactions also take place. Zeolite Ti–Alβ has been shown by Derouane et al. [20] to be an effective catalyst in the oxidation of cyclic alkenes. Using non-aqueous hydrogen peroxide as oxidant, methanol or ethanol as protic solvent, and a reaction temperature in the range 40–70°C, optimal substrate conversion and product selectivity to glycol monoether was obtained. However, the acidic properties can be neutralized in several ways like the ion-exchange with alkali metals Li, Na, K, Mg and Ba and the use of basic solvent, etc. and highly selective oxidation can be performed [15,21,22].

Recently, a direct crystallization of Na-containing Tiβ zeolite with high oxidation activity has been carried out in the presence of TEAOH and steam by the dry-gel conversion technique [23–25]. The catalytic activity of the only calcined Tiβ (H_2SO_4-unwashed) in the oxidation of cyclohexene with aqueous H_2O_2 could reach the level of about 100% in the conversion and selectivity of H_2O_2 to the oxidized products, which was somewhat different from the case in the Na–TS-1 reported by Khouw and Davis [16]. It has been observed that the existence of small amounts of Na was not a real hindrance to the insertion of Ti into the β framework but a requisite to the crystallization of Tiβ phase, and to the activity of Tiβ synthesized under the optimum conditions. The presence of Al in these catalysts resulted in the production of glycols, but the catalysts with higher Na content exhibited higher selectivity to the epoxide; however, without exception, the H_2SO_4-washed Tiβ catalysts preferred glycols and ethers. In current study, our interests are mainly focused on the characteristics of epoxidation of bulkier cyclic alkene substrates with aqueous H_2O_2 and *tert*-butyl hydroperoxide (TBHP) on the calcined Na–Tiβ (H_2SO_4-unwashed) synthesized by the dry-gel conversion technique and on the factors influencing the selectivity to epoxide, such as time, conversion, composition, solvent and oxidant, etc.

2. Experimental

2.1. Synthesis

The Tiβ zeolites were synthesized according to the methods reported elsewhere [23]. The analyses showed that the resulting solids contained a little amount of Na and Al. Amorphous SiO_2/TiO_2 was obtained from a failed synthesis. Nanosized TS-1 was synthesized according to the procedure reported in the reference [26]. All Na-containing Tiβ catalysts used in the reactions did not undergo further acid-treatment. X-ray diffraction (XRD) profiles of all of Tiβ samples displayed XRD peaks of typical β crystal phase, and the crystallinity of samples decreased along with the increase of Na content. In unspecified cases, Tiβ-1 with a BET surface area of 589.3 m^2/g (calcined at 520°C for 10 h in air), was used as the catalyst to investigate the effect of various factors on the epoxidation of cyclic alkenes with H_2O_2 and TBHP, its composition and physical properties have been shown in Table 1.

Table 1
Comparison of the catalytic activity of Na-containing Tiβ zeolites with TS-1 and amorphous SiO_2/TiO_2 catalysts for the oxidation of cyclohexene with H_2O_2[a]

Sample	Gel			Calcined			Crystallinity[b] (%)	Size[c] (nm)	H_2O_2 selectivity (%)	CON[d] (mol%)
	Si/Al	Si/Ti	Si/Na	Si/Al	Si/Ti	Si/Na				
Tiβ-1	331	30.4	98.4	352	31.3	94.4	81.5	30	100	30.4
Tiβ-2	332	30.2	49.9	324	28.4	49.3	37.2	49	69.1	21.0
Tiβ-3	331	30.2	141.4	323	31.0	151.8	80.7	31	97.0	29.5
	477	30.8	143.9		n.d.		Amorphous	Amorphous	2.6	0.8
TS-1				>5000	79.0	∞	100	150	5.9	1.8
TS-1				>5000	117.0	∞	100	87	6.5	2.1

[a] The solvent used is methanol.
[b] Relative crystallinity (%).
[c] Average crystal size (nm).
[d] Conversion of cyclohexene to oxidized products (mol%).

2.2. Characterization

The XRD patterns of solid samples were recorded by X-ray diffractometer (Cu target/40 kV/20 mA, MO3X/MAC/Nippon). The UV–VIS spectra were automatically recorded by a Hitachi U-4000 UV–VIS reflectance spectroscopy. The average crystal size of the samples was calculated in terms of SEM pictures (FE-SEM, Nippon). The samples were pretreated overnight at 393 K under vacuum prior to the SEM determination. The elemental content analyses were performed by ICAP-575 atomic emission spectrophotometer (Japan) for Ti and Al, and by flame spectrometry for Na. BET surface area of Tiβ sample was measured on Micromeritics ASAP-2000 at a bath temperature of 77.35 K. The degassed and activated pretreatment was carried out for over 10 h at 623 K prior to the adsorption analysis.

2.3. Catalytic reaction

Typically, organic substrate 33 mmol, H_2O_2 10 mmol (31 wt.% aqueous solution), solvent 20 ml, catalyst 200 mg were added in a glass round-bottom flask, and the reaction mixture was refluxed at 333 K in a water bath for 3 h or longer under vigorous stirring. The epoxidation of alkenes with TBHP (69 wt.% aqueous solution) was conducted at 333 K for 5 h. After completing reaction, the liquid products were separated from the solid catalyst by filtration and analyzed by gas chromatography using an OV-1 capillary column fitted with FID. Cycloheptanone or cyclohexanone was used as an internal standard to quantify the content of all constituents. The conversion of organic substrates (mol%) (CON) $=$ (total moles of the oxidized products/moles of substrate) $\times$ 100%, where the highest conversion is 30.4 mol% for organic substrate based on the molar ratio of substrate to oxidant. The conversion of H_2O_2 (CH) and TBHP were analyzed by $Ce(SO_4)_2$ titration, and the selectivity of oxidant to oxidized products (SH) was calculated.

3. Results and discussion

3.1. Epoxidation of cyclohexene

3.1.1. Effect of reaction time and conversion

In the oxidation of cyclohexene with H_2O_2, when CH_3OH (MeOH) is used as the solvent, a complicated distribution of products can be detected. They include epoxide (EP), glycols (glycol), monomethylglycol ethers (ether) and 2-cyclohexene-1-ol $+$ 2-cyclohexene-1-one (CHO), in which EP is a target product, others are acid-catalyzed by-products, in some cases glycol and ether are calculated as GLYS.

In order to test the efficiency of Tiβ zeolites in the oxidation of cyclohexene with H_2O_2, a comparison between Tiβ and TS-1 has been made, and the data are shown in Table 1. When this reaction is performed

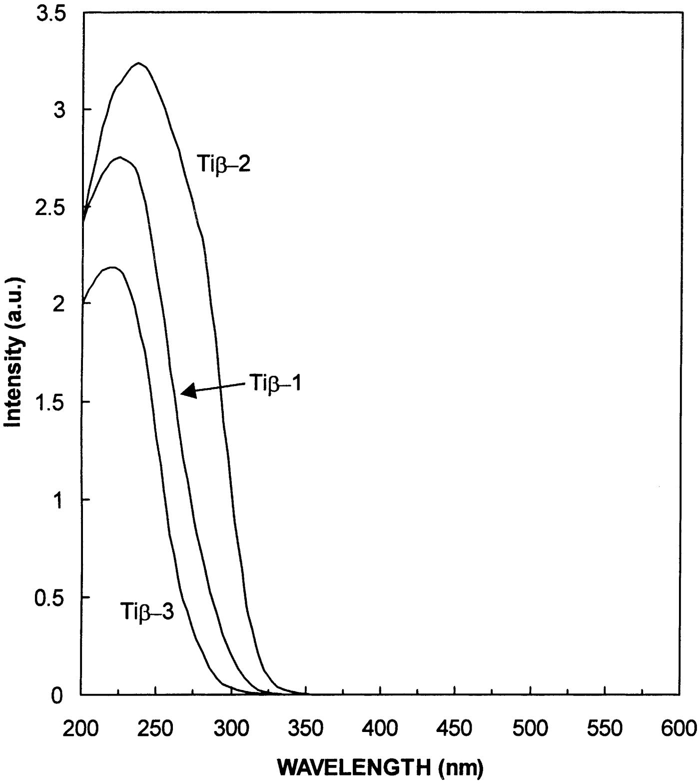


Fig. 1. UV–VIS spectra of three Na-containing Tiβ zeolites having different Si/Na ratios.

over TS-1, either H_2O_2 selectivity or conversion is very low, ascribed to the severe restriction of TS-1 for the diffusion of bulky cyclohexene molecules into its pores. The reduction of TS-1 crystal particles from 150 to 87 nm does not show any remarkable change in the activity and selectivity of the catalyst, this may be because using small crystal size TS-1 cannot still overcome the diffusion problems. For this reaction, the activity of amorphous SiO_2/TiO_2 is extremely low, which is understandable as Ti is not present in the framework of tetrahedra SiO_4. However, it is seen that all of Tiβ samples show excellent activities, and almost 100% of H_2O_2 are efficiently converted. It is because the crystal sizes of Tiβ zeolites are smaller than 50 nm, and the majority of Ti is localized in the lattice of tetrahedra SiO_4 as characterized by UV–VIS spectra in Fig. 1. When the Si/Na molar ratio is 94.4 (Tiβ-1) or 151.8 (Tiβ-3), only a strong band at ca. 220 nm can be observed. While the Tiβ-2 with $Si/Na = 49.3$ contains some extra framework Ti as its UV–VIS spectrum displays a broad shoulder at ca. 285 nm. The anatase band, which occurs at 320 nm, seems to be superimposed on this band. The results suggest that the more the amount of sodium present in the starting gel, the less efficient the incorporation of Ti into the framework of β zeolite.

Using the Tiβ-1 catalyst, the effect of reaction time on the conversion of cyclohexene and H_2O_2 as well as the relationship between product distribution and conversion of cyclohexene was investigated in detail. Fig. 2 shows that increasing the batch reaction time gradually improves the conversion of cyclohexene and H_2O_2 to approach their respective equilibrium values 21.9 (CON) and 84 (CH) mol% within 5 h. However with the reaction time, the selectivity of H_2O_2 to oxidized products gradually decreases from 100 to 86.4% (SH), showing that the decomposition of unreacted H_2O_2 is increasing. Longer reaction time should be

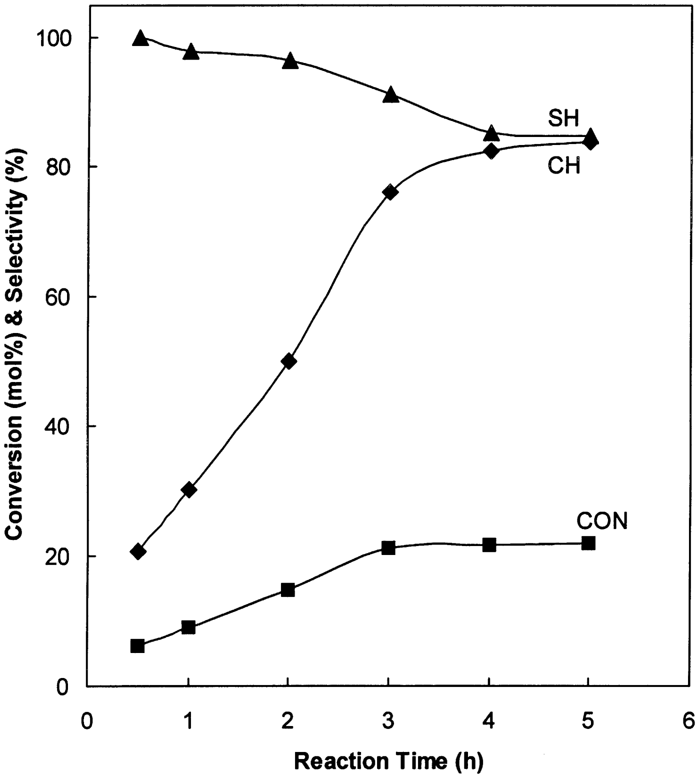


Fig. 2. Effect of reaction time on the conversion of cyclohexene and H_2O_2 in MeOH solvent as well as the selectivity of H_2O_2 to oxidized products.

avoided because in oxidations with H_2O_2 as oxidant, organic substrates can be repeatedly separated and recycled; however, the recycling of H_2O_2 is very difficult to realize due to unreacted decompositions of H_2O_2.

Fig. 3 shows that when the conversion of cyclohexene is limited to 6.2 mol%, the selectivity to EP is 90% and that to glycol, ether and CHO is less than 10%. However, the cyclohexene conversion is increased from 6.2 to 22.3 mol%, a drastic drop in the selectivity of EP to 20% is clearly observed. This shows that for the oxidation of cyclohexene with H_2O_2, the epoxide is the preliminary reaction product, while ether, glycol and CHO are secondary reaction products. It is worthwhile to note that Tiβ in these reactions contains small amount of alumina, leading to Brönsted acidic sites that catalyze secondary reactions on the epoxide to yield glycol, ether and CHO, in agreement with the observations in the literatures [1,4,20].

3.1.2. Effect of catalyst compositions

The introduction of Na into catalysts is an effective route to equilibrate the surface acid sites of Tiβ zeolites; however, the content of Na in the sample cannot be too high so that the activity of catalyst is retarded, as shown in Fig. 4. When the Si/Al ratio and the Si/Ti ratio are fixed at 330 and 31.3, respectively, the effect of the Si/Na ratio has been investigated. Fig. 4 illustrates that the selectivity to epoxide decreases gradually with increasing the Si/Na molar ratio. As the Si/Na ratio is 49.3, the selectivity of epoxide in the products is about 22.7%; however, less cyclohexene (ca. 21.3 mol%) is converted to the products because of the restricted Ti amount inserted into the framework. In this case, the conversion of H_2O_2 is the lowest (ca. 76 mol%), about 91.2% of H_2O_2 is selectively utilized to oxidized products. When the Si/Na ratio is increased to 94.4, the selectivity of EP drastically reduces to 1.2%, about 95.9% of the products are glycol and ether. This

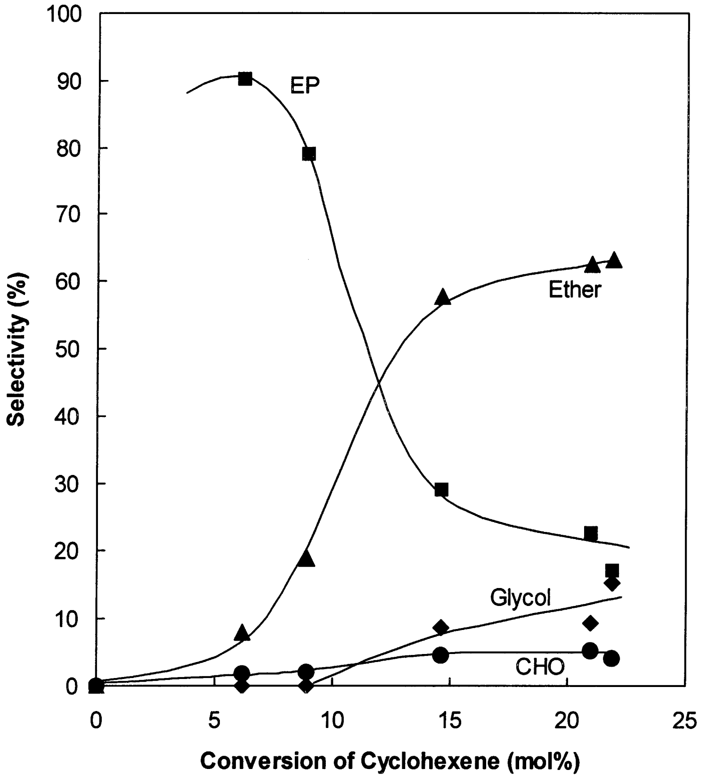


Fig. 3. Effect of the conversion of cyclohexene in MeOH solvent on the selectivity of oxidized products EP, glycol, ether and CHO.

increase in the Si/Na ratio, however, leads to a remarkable enhancement in the activity of catalyst, in which more cyclohexene (ca. 30.4 mol%) is converted to the products, and nearly 100% of H_2O_2 is selectively converted to oxidized products. With an increase of the Si/Na ratio to 151.8, the conversion of cyclohexene and H_2O_2 decrease to 29.5 and slightly to 99.4 mol%, respectively. A further increase of the Si/Na ratio to 243.9 results in a further reduction of conversion of cyclohexene and H_2O_2 to 29 and 96 mol%, respectively. Whereas in the range of the Si/Na ratio from 94.4 to 243.9 the unreacted decomposition of H_2O_2 is totally avoided, and the selectivity to glycol and ether (95.8–95.9%) and to EP (1.1–1.7%) are kept almost unchanged. The results have shown that lower Si/Na ratio (i.e. higher Na amount) is conducive to the yield of epoxide compounds. This is because the presence of trace amount of Na partially neutralizes the surface acidity of Tiβ caused by framework Al, and reduces the possibility of acid-catalyzed secondary reactions, resulting in an increase in the selectivity to epoxide. The results also show that sodium has multiple roles, it affects either the synthesis or the activity and the selectivity of Tiβ zeolites.

When the Si/Na ratio is fixed, the Si/Ti ratio is another important factor influencing the conversion of cyclohexene and H_2O_2 and the selectivity to products (Fig. 5). Based on the data in Fig. 5, the Si/Ti ratio of about 31.3 is the optimal value for the high conversion of cyclohexene and H_2O_2. In this case, approximately 100% of H_2O_2 is converted to the products, and the conversion of cyclohexene reaches the maximum of 30.4 mol%; however, the selectivity to EP is the lowest only 1.2 and 95.9% of products are glycol and ether. As the Si/Ti ratio is decreased to 17.8, the selectivity to epoxide in the products is still kept at 1.6%; however less cyclohexene (ca. 26.5 mol%) and H_2O_2 (ca. 92 mol%) are converted to the products, and about 95% of H_2O_2 is selectively utilized to oxidized products as the catalyst obtained contains

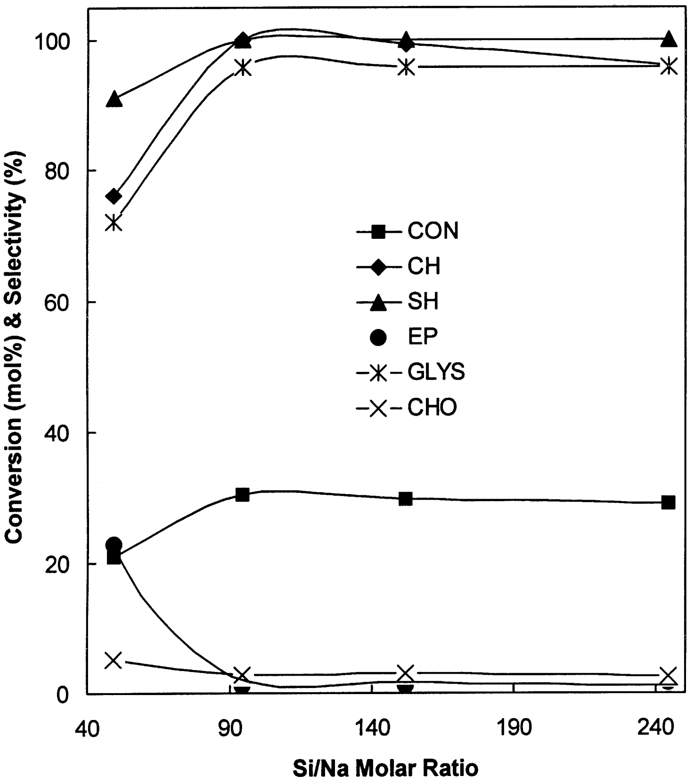


Fig. 4. Effect of the Si/Na molar ratio in the catalysts on the conversion of cyclohexene in MeOH solvent and H_2O_2 as well as the selectivity of H_2O_2 and oxidized products.

some extra framework TiO_x. A peak for the selectivity to epoxide (19.5%), appears at the Si/Ti ratio of about 55.5, corresponding to the smallest distribution of GLYS + CHO. However, the conversion of cyclohexene is only 16.2 mol%, nearly equivalent to half of the conversion at the Si/Ti ratio of 31.3. At this point, merely 54 mol% of H_2O_2 is converted, while 100% of H_2O_2 is efficiently utilized. With an increase of the Si/Ti ratio from 55.5 to 78.4, the conversion of cyclohexene and H_2O_2 reduce continually from 16.2 to 10.2 mol% and from 54 to 47 mol%, respectively; the selectivity to EP decreases from 19.5 to 12.3% and the utilization of H_2O_2 from 100 to 72%. This implies that the content of Ti, Na and Al must be mutually optimized due to their co-existence in the same catalyst so as to obtain the most active catalyst having the high selectivity of epoxide.

The effective insertion of Ti into SiO_4 framework to form Ti-containing tetrahedra has been very important for the enhancement of oxidation activity of catalyst. In most cases, the presence of Na takes a real hindrance to the incorporation of Ti into zeolite framework. While using dry-gel conversion technique to synthesize Tiβ, appropriate quantity of sodium does not have a real negative effect on the formation of Tiβ with high oxidation activity. The results in the preceding context have shown the effect of the Si/Na ratio and the Si/Ti ratio on the conversion of cyclohexene and the selectivity to epoxide. Therefore, the effect of the Ti/Na ratio deserves studying and the data are depicted in Fig. 6. The conversion of cyclohexene increases gradually as the Ti/Na molar ratio increases from 0 to 3, reaches the optimal value of 30.4 mol% at the Ti/Na ratio of about 3, and then slowly decreases as the Ti/Na ratio increases further. The change of selectivity to epoxide with the Ti/Na ratio is totally different from that of conversion. For the selectivity to epoxide, a sharp peak near to 26.1% appears in the

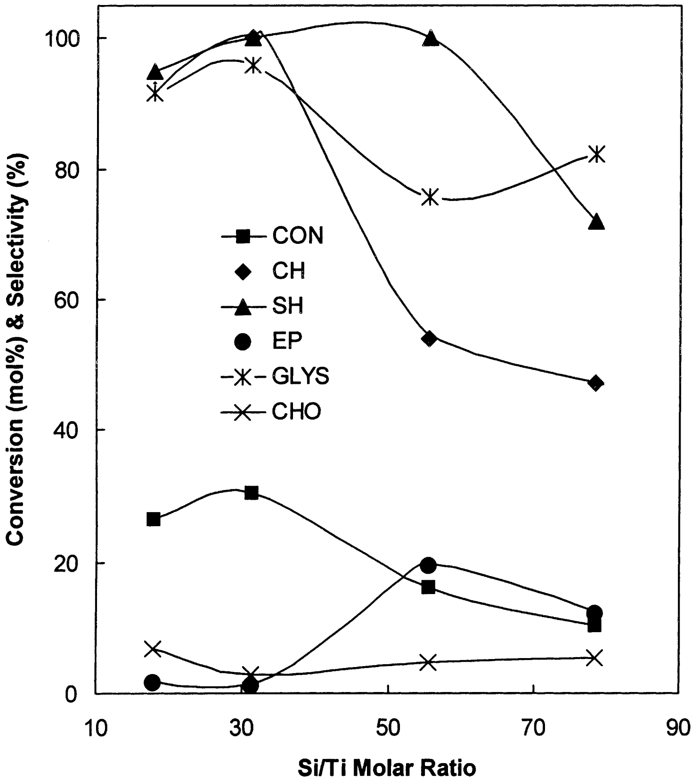


Fig. 5. Effect of the Si/Ti molar ratio in the catalysts on the conversion of cyclohexene in MeOH solvent and H_2O_2 as well as the selectivity of H_2O_2 and oxidized products.

Ti/Na ratio ranging between 1.5 and 1.7, where the possibility of acid-catalyzed secondary reactions could be limited to the largest extent due to neutralized surface acidity. However, in this case the conversion of cyclohexene is merely 22.5 mol% due to the restricted Ti amount inserted into the framework affected by the existence of Na. Although as the Ti/Na ratio is about 3, the conversion of cyclohexene reaches the highest, the selectivity to epoxide drops at six-fold to <4%. This result suggests that the Ti/Na molar ratio be a critical parameter for the selective acquirement of epoxide over Na–Tiβ catalyst.

3.1.3. *Effect of solvent*

It is well known that the choice of suitable solvent can play a critical role on the activity and selectivity in the liquid-phase oxidations over titanium zeolites. The oxidation of cyclohexene with H_2O_2 was performed on the Tiβ-1 sample using various protic and aprotic solvents having different polarity (i.e. different dielectric constants). These solvents are chosen to form a single phase with organic substrates and hydrogen peroxide solution, so that the mass transfer problems associated with dissolubility are avoided. The solvents used in the experiments are CH_3OH (MeOH), C_2H_5OH (EtOH), *tert*-C_4H_9OH (Bu^tOH), CH_3CN (MeCN), CH_3COCH_3 (MeCOMe) and $CH_3COC_2H_5$ (MeCOEt), of which MeOH, EtOH and Bu^tOH are protic solvents, the other three solvents are aprotic. The decrease order of dielectric constants is for protic solvents: Bu^tOH (10.9) < EtOH (24.5) < MeOH (32.7), and for aprotic solvents: MeCOEt (18.5) < MeCOMe (20.7) < MeCN (37.5), respectively.

It can be observed from Table 2, that the conversions of cyclohexene and H_2O_2 as well as the selectivity of H_2O_2 with protic solvents are higher than those with aprotic ones, which can be ascribed to the positive

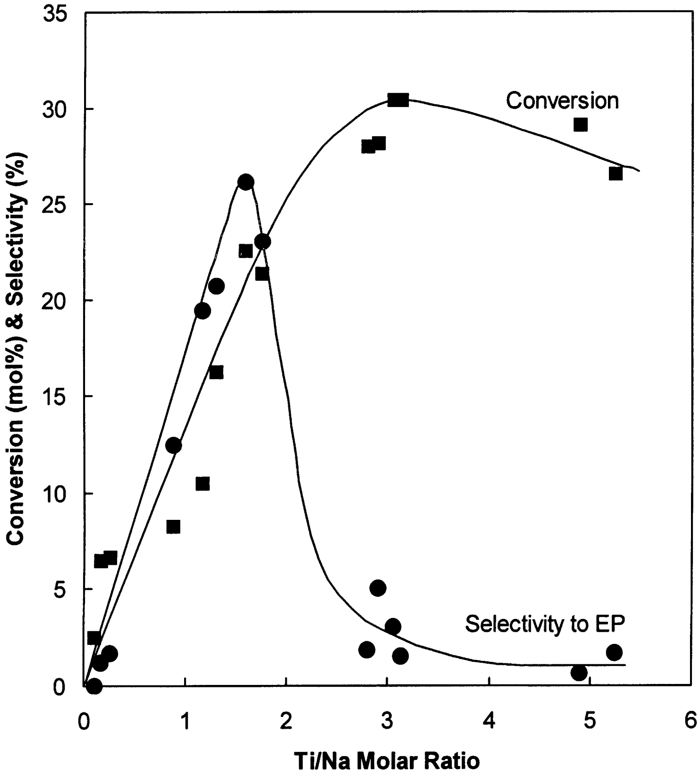


Fig. 6. Effect of the Ti/Na molar ratio in the catalysts on the conversion of cyclohexene in MeOH solvent and the selectivity of epoxide in the oxidized products.

effect of protic solvents on the formation of a cyclic intermediate over the surface of catalyst prior to the coordination of alkene to the Ti-peroxo complex [14,24]. The activity order observed is for protic solvents: Bu^{t}OH < EtOH < MeOH as a result of decreasing electrophilicity and increasing steric constraints of surface intermediate [14]. While for aprotic solvents, the activity order is observed to be MeCOEt < MeCOMe < MeCN which is opposite to those observed by Corma [27] suggests that Tiβ prepared in this system is relatively hydrophobic, as is the case of Na and Al-free TS-1. This observation could be due to the larger aprotic solvent molecules being strongly adsorbed onto the hydrophobic surface of zeolite pores, thereby blocking the pores and partially covering the Ti catalytic sites.

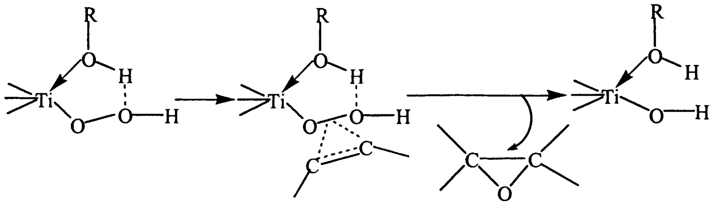


Fig. 7 shows the effect of various solvents on the distribution of oxidized products. In all solvents tested, the selectivity to epoxide, when MeCN is used as the solvent, is the highest up to 59% about 49 times as much as that obtained using MeOH as the

Table 2
Effect of solvents on the conversion of cyclohexene and H_2O_2 as well as the selectivity of H_2O_2 to oxidized products

Solvent	Polarity	Dielectric constant	Conversion (mol%)		H_2O_2 selectivity (%)
			Cyclohexene	H_2O_2	
MeOH	Protic	32.7	30.4	100	100
EtOH	Protic	24.5	27.9	94	98
Bu^tOH	Protic	10.9	21.7	74	98
MeCN	Aprotic	37.5	17.6	70	86
MeCOMe	Aprotic	20.7	19.0	72	87
MeCOEt	Aprotic	18.5	21.1	74	94

solvent; while the selectivity to epoxides for other solvents are less than 3%. The higher selectivity to epoxide obtained using MeCN as solvent is a result of decreasing acidity caused by the solvent coordination of the basic acetonitrile molecules [27] and subsequently decreasing the extent of acid-catalyzed secondary reactions. In the cases of MeOH and EtOH as the protic solvents, majority of products is ether; however, when Bu^tOH is used as the solvent, majority of products is still glycol. Firstly, it is because the reaction between glycol and MeOH or EtOH can be easily acid-catalyzed to form glycol ether as a result of strong polarity of intermolecules. On the other hand, this phenomenon may be ascribed to the restrictions imposed by the zeolite pores, that seriously affects adsorption–diffusion–desorption process and is

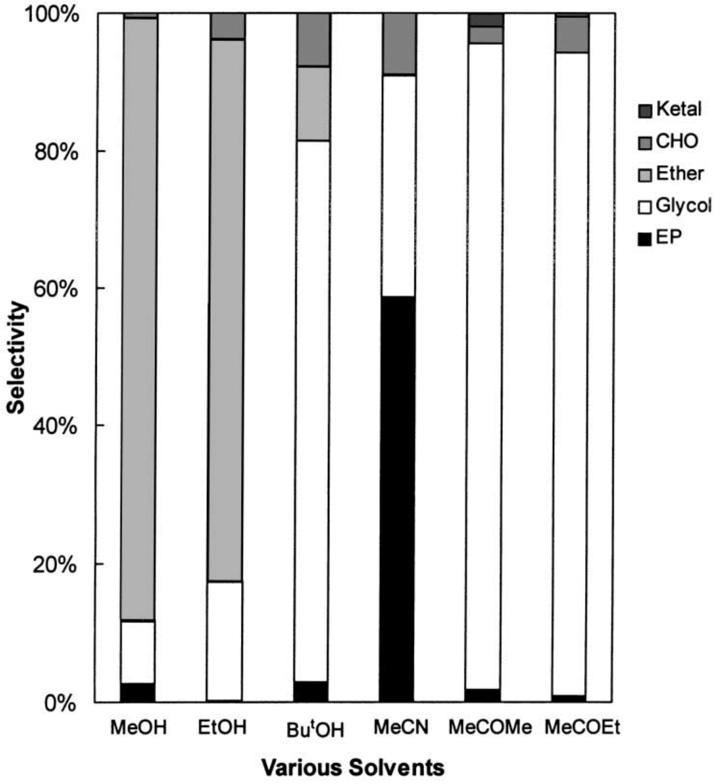


Fig. 7. Effect of the solvents on the selectivity of oxidized products: EP, glycol, ether, CHO and ketal.

the difficulty in the opening of the epoxides rings by bulky alcohols in the confines of the pore (restricted transition state shape selectivity) [20]. In the case of three aprotic solvents, the secondary reaction from glycol to ether cannot take place; however, it should be noted that in the reactions using MeCOMe and MeCOEt as the solvents, ketone could react with glycols to form cyclic ketal.

3.2. Epoxidation of cyclic alkenes

3.2.1. Dilute H_2O_2 as oxidant

As shown in Figs. 8 and 9, the epoxidation of several cyclic alkenes inclusive of cyclopentene (C5), cyclohexene (C6), cycloheptene (C7), cyclooctene (C8) and cyclododecene (C12), with H_2O_2 has been studied using CH_3OH as the solvent. Amongst cyclic alkenes tested, C6 is the most reactive, 30.4 mol% of cyclohexene and approximately 100 mol% of H_2O_2 can be selectively converted to oxidized products. Generally, the reactivity (CON) of cyclic alkenes decreases with increasing carbon number from C6 to C12, while the reactivity of cyclopentene (C5) is lower than that of cyclohexene (C6). The reactivity of cyclododecene (C12) is the lowest, possibly due to the low diffusivity of cyclododecene and the corresponding products in the pores. The conversion of H_2O_2 (CH) displays a similar regularity to the change of reactivity of alkenes with carbon number, however, the change in the selectivity of H_2O_2 (SH) is different. For the oxidations of C6 to C12 cyclic alkenes, approximately 100% of H_2O_2 are effectively utilized. While for the oxidation of C5, although the conversion of H_2O_2 is close to 100 mol%, merely 66% of H_2O_2 is selectively utilized. As a comparison, the oxidation of linear 1-dodecene (L-C12) with H_2O_2 is conducted as well. The reactivity of L-C12 is found to be slightly higher than that of

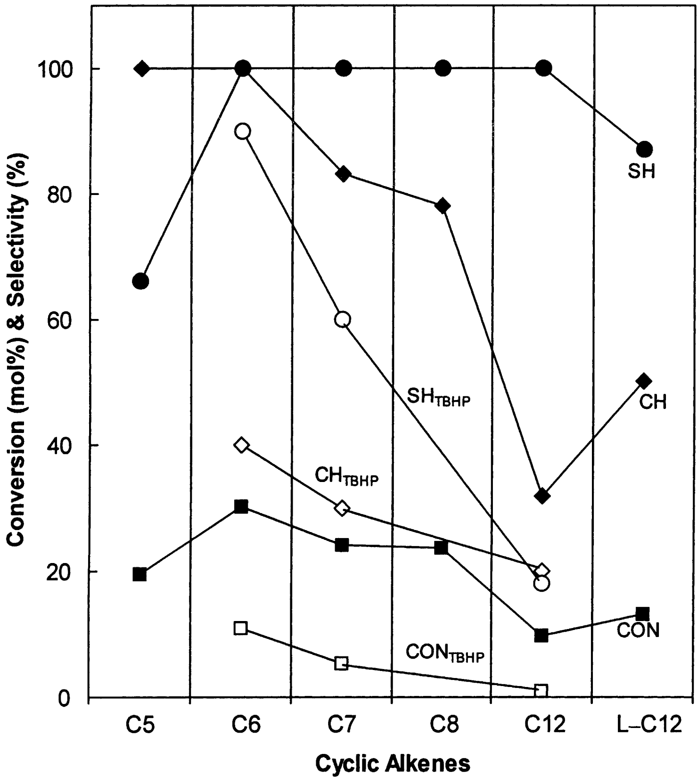


Fig. 8. The conversion of cyclic alkenes and oxidants in MeOH solvent as well as the selectivity of oxidants to oxidized products using H_2O_2 and TBHP as the oxidants.

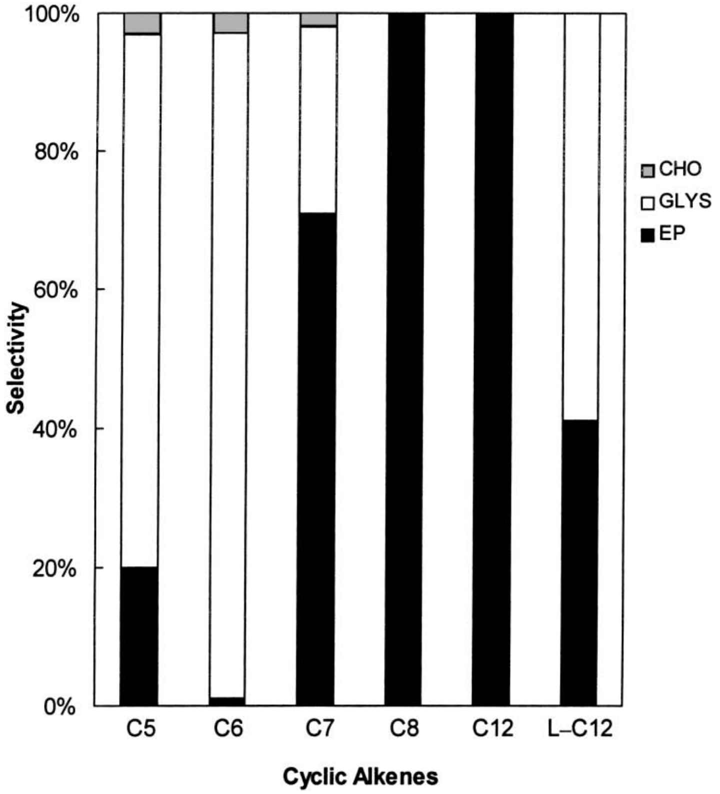


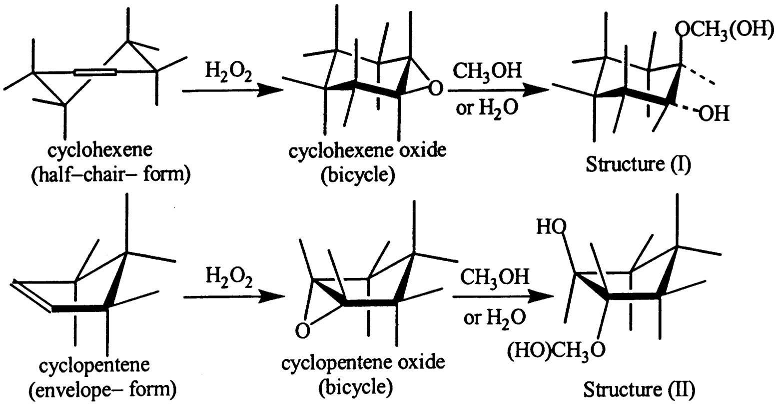
Fig. 9. The selectivity of oxidized products inclusive of EP, GLYS and CHO in the epoxidation of cyclic alkenes with H_2O_2 using MeOH as the solvent.

cyclic C12, possibly due to the fact that the diffusivity of linear alkene in the large pore of Tiβ is higher than that of cyclic alkene with the same carbon number. The conversion of H_2O_2 is higher for the oxidation of L-C12 than for C12, however, the efficient utilization of H_2O_2 is lower.

The selectivity of cyclic epoxide is found to display a reduction tendency in the following order: $\mathrm{C12} \approx \mathrm{C8}\,(100\%) > \mathrm{C7}\,(71\%) > \mathrm{C6}\,(1.2\%)$ with carbon number. For cyclohexene, the ring-opening products of epoxide are obtained almost exclusively. In contrast, for cyclooctene and cyclododecene almost 100% of substrates are quantitatively epoxidized to epoxide. Cycloheptene gives rise to an intermediate selectivity for epoxide, a high selectivity up to 71% to epoxide is attained. The results suggest that bulkier alkene oxides be prevented from solvolysis which requires bulkier transition state in the sterically restricted pores of Tiβ, in agreement with the results reported by Dartt et al. [28]. Additionally, for the oxidations of C5–C7, certain amount of CHO impurities can be detected; however, for C8, C12 and L-C12, those disappear totally. Similar to the difference in the reactivity, the selectivity of C12 and L-C12 to epoxide also shows a distinct difference: $\mathrm{L\text{-}C12}\ (41.1\%) < \mathrm{C12}\,(100\%)$. It suggests that the possibility of cyclic alkene oxide approaching the acid site in the pore of Tiβ be less than that of linear alkene oxide due to the steric hindrance, resulting in a high ring-opening conversion of linear alkene oxide catalyzed by acidity to glycol. However, an exception is observed that the selectivity of C5 to epoxide (20%) is much higher than that of C6 to epoxide (1.2%).

Most likely, there are two explanations responsible for the lower reactivity of and the higher selectivity to epoxide of cyclopentene (C5) than cyclohexene (C6).

Firstly, low boiling point (44°C) of cyclopentene leads to its low dissolubility into the reaction mixture at the reaction temperature of 333 K, resulting in the reduction in its conversion. Another explanation could be relevant to the following reasoning.



In the reaction, the conformation of cyclohexene and cyclopentene should take half-chair-form and envelope-form, respectively. As a result of the easier reversal and deformation of chair-form conformation than envelope-form conformation, cyclohexene molecules probably approach the active Ti sites in the channels of the large pore Tiβ during diffusion process to form the transition state more easily than cyclopentene molecules, resulting in the difference in the reactivity of both molecules. After the *cis*-addition of their double bonds with [O], bicyclic cyclohexene oxide with a chair-form conformation and bicyclic cyclopentene oxide with an envelope-form conformation are formed. Under further acidic catalysis, their bicyclic epoxides are converted to the corresponding glycols or glycol monomethylethers through *trans*-addition with CH_3OH or H_2O. In the structure of cyclohexyl glycol or cyclohexyl glycol monomethylether (I), one of either methyl group and hydroxyl group or both hydroxyl groups occupies the axial position, the other one is in the equatorial position to form a stable chair-form conformation. In contrast, the intrinsic repulsive interaction among radicles in the conformation of the structure (II) is stronger than that of the structure (I), this leads to the relative difficulty of conversion of cyclopentene oxide into cyclopentyl glycol or cyclopentyl glycol monomethylether (II). As a result, an exception observed that the selectivity of C5 to epoxide (20%) is much higher than that of C6 to epoxide (1.2%), is possibly due to the above reasoning.

3.2.2. TBHP as oxidant

TBHP as the oxidant is often used in the homogeneous oxidation; however, it is inactive for the oxidation on TS-1, owing to the diffusion hindrance of larger TBHP molecules into narrow channels of the MFI structure, whereas such steric restrictions could be overcome as Tiβ was used as the catalyst [7]. As shown in Figs. 8 and 10, the epoxidation of three cyclic alkenes (C6, C7 and C12) with TBHP on the Tiβ-1 catalyst has been studied using CH_3OH as the solvent. The reactivity of cyclic alkenes (CON_{TBHP}) and TBHP (CH_{TBHP}) as well as the selectivity of TBHP (SH_{TBHP}) towards oxidized products decrease with increasing carbon number: C6 > C7 > C12, similar to the case of H_2O_2 as the oxidant. When TBHP is used as the oxidant, the oxidation rate of cyclic alkenes is remarkably slower than that in the case of H_2O_2, in which even though the reaction time is prolonged to 5 h, the conversion of substrates are still rather low. In contrast to H_2O_2 as the oxidant, when TBHP is used as oxygen donor, the reactivity of C6, C7 and C12 shows a drastic reduction, their respective conversion decreases down to 10.9, 5.5 and 1.1 mol%. The conversion of TBHP is reduced as well, in particular the utilization of TBHP is greatly reduced down, showing that the unreacted decomposition of TBHP has increased. These results suggest that steric restrictions

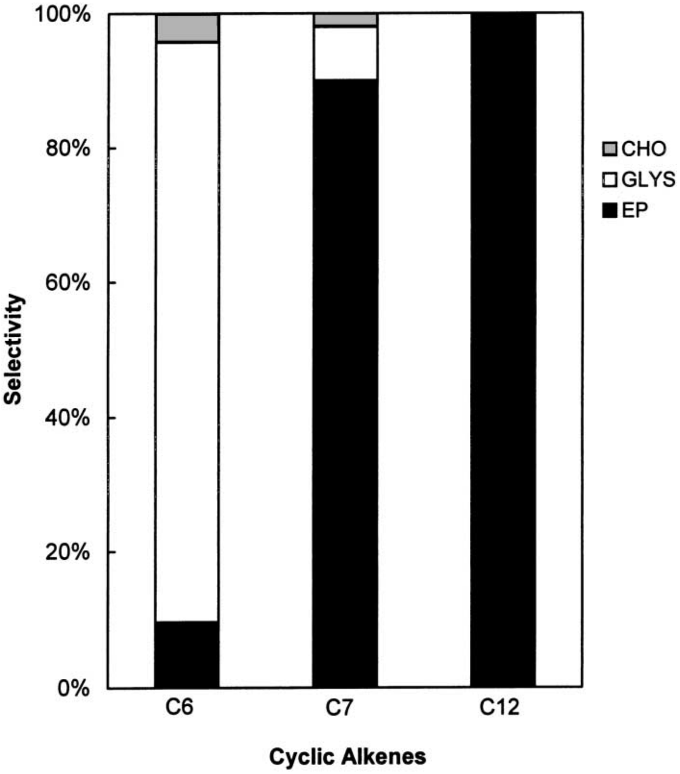


Fig. 10. The selectivity of oxidized products inclusive of EP, GLYS and CHO in the epoxidation of cyclic alkenes with TBHP using MeOH as the solvent.

inside the pores of Tiβ be enhanced when using a bulkier oxidant such as TBHP, further decreasing the possibility of substrate molecules approaching oxygen donor [7].

Fig. 10 shows that TBHP as the oxidant is more beneficial to the selective production of epoxide than H_2O_2, and the selectivity to EP displays a remarkable increase with increasing carbon number: C6 (9.7%) $<$ C7 (90%) $<$ C12 (100%). We assume a similar mechanism is operative for the epoxidation of cyclic alkenes with H_2O_2 and TBHP. Obviously, the transition state involving the Ti–OOR and cyclic alkene must be much bulkier than that relating to the Ti–OOH and alkene. This characteristic significantly retards the reaction rate of cyclic alkenes with TBHP, further decreasing the possibility of acid-catalyzed secondary ring-opening reaction of epoxide molecules.

4. Conclusion

The Na–Tiβ zeolites synthesized in this system have shown high activities for the liquid-phase oxidations of cyclic alkenes with H_2O_2 without undergoing further acid-treatment. Many factors such as the Si/Na ratio, the Si/Ti ratio, and the Ti/Na ratio have been found to take effects on the conversion of cyclohexene and H_2O_2 and the selectivity of epoxide. Lower conversion (about 6.2 mol%) of cyclohexene has been shown to improve the selectivity of epoxide (about 90%). The use of the solvent having bigger dielectric constant is very helpful for the enhancement of reactivity of substrate, in particular under identical conditions MeCN is an optimal choice for improving the selectivity of epoxide up to 59% about 49 times as much as that using MeOH as the solvent. The reactivity of cyclic alkenes decrease with increasing carbon number from C6 to C12, the exception of C5 has been suggested to be relevant to its low dissolubility and steric conformations of reactant and products molecules. While the change of the selectivity to their epoxides can be put in order of $C12 \approx C8\,(100\%) > C7\,(71\%) > C5\,(20\%) > C6\,(1.2\%)$, where bicyclic cyclohexene oxide is the most easily ring-opened to form acid-catalyzed secondary products. The reactivity of linear alkene is higher than cyclic alkene with the same carbon number, but the selectivity to epoxide is lower. In contrast to H_2O_2 as the oxidant, TBHP greatly retards the reactivity of C6, C7 and C12, and is more beneficial to the selective production of epoxide than H_2O_2.

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