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Epoxidation of alkenes and their derivatives over Ti-YNU-1

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ABSTRACT

The catalytic properties of Ti-YNU-1 for the epoxidation of various alkenes and their derivatives have been investigated in detail, and further were made a comparison with those of Ti-Beta. The much higher efficiency of Ti-YNU-1 than Ti-Beta was observed in catalyzing the epoxidation of alkenes and their electron-rich analogues. Although it was less active in the epoxidation of α,β-unsaturated ketones, it showed much higher stability. In contrast, Ti leaching from the framework sites occurred to Ti-Beta, and the leaching degree increased with the carbon number of ketones. It was also shown that the catalytic conditions, including the Ti content in samples, H_2O_2/substrate ratio, reaction temperature and time, acid washing and catalyst amount, significantly influenced the activity, selectivity and H_2O_2 efficiency. Co-oxidation of different alkenes led to the activity and epoxide selectivity being different from those obtained in the oxidation of single olefin as a result of the differences in adsorption properties of substrates over various titanosilicates, which affected the diffusion of substrate molecules and accounted for the unique shape-selectivity of Ti-YNU-1.

1. Introduction

The epoxidation of alkenes is one of the key steps in functionalizing hydrocarbons and rapidly building functionality into a range of molecules. This is because epoxides are highly useful intermediates for the manufacture of many important commercial products, such as corrosion-protecting agents, pharmaceuticals, additives, etc. [1,2]. Their selective synthesis is of considerable academic and industrial interest.

The industrial production of epoxides from the oxidation of alkenes (except for light alkenes) is mostly using homogeneous catalysts such as peracids. However, this inevitably produces a lot of wastes, polluting the environment. From the viewpoint of sustainable and green chemistry, heterogeneous catalysts would be attractive since they offer the advantages of facile catalyst separation, possible catalyst recycle and sometimes high selectivity. In addition, there is a strong need for employing safe and clean oxidants, e.g. O_2 and H_2O_2 which give water as the only by-product. It has been shown that titanosilicates are the most efficient heterogeneous epoxidation catalysts. TS-1 exhibits high catalytic activity and selectivity in the epoxidation of propylene using aqueous H_2O_2 as an oxidant [3]. However, its small pore opening restricts it to the epoxidation of linear alkenes.

To overcome the steric limitation of TS-1, Ti-Beta and mesoporous titanosilicates have been developed [4–7]. Indeed, these materials have been proved to efficiently catalyze the oxidation of bulky substrates such as cyclododecene, cyclohexene, cyclohexane and their substituted derivatives, compared with TS-1 [5,7,8]. Nevertheless, the presence of weak acid sites in Ti-Beta, and the amorphous nature and resultant strong hydrophilicity of mesoporous materials significantly decrease the reactivity and epoxide selectivity when H_2O_2 aqueous solution serves as an oxidant [9–11]. Although tripodal titanium silsesquioxane complexes immobilized in polydimethylsiloxane membrane, silica-supported titanium oxide catalysts prepared by the controlled calcination of Ti-bridged polyhedral oligomeric silsesquioxanes and dititanium-containing 19-tungstodiarsenate (III) were used to catalyze the epoxidation of alkenes, the epoxide selectivity, the catalyst stability against Ti leaching and/or the use of *tert*-butyl hydroperoxide were still problems [12–14]. Recently, we successfully synthesized a new titanosilicate of Ti-YNU-1 that contains 12-membered ring (MR) interlayer pores. This material shows much higher activity, epoxide selectivity and stability against Ti leaching than Ti-Beta in the oxidation of cycloalkenes [15,16]. Here, we give a detailed investigation of this material for the oxidation of alkenes and their derivatives, which includes three parts: (1) the influence of catalytic conditions on the epoxidation of cycloheptene; (2) shape-selective

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Table 1
Catalytic results of Ti-YNU-1 and Ti-Beta with different Ti contents for the oxidation of cycloheptene[a].

Samples	Si/Ti	TON	Conv. (%)	Selectivity (%)		H_2O_2 eff. (%)[d]
				Epoxide	Others	
Ti-YNU-1-267[b]	267	536.9	66.7	92.3	7.7	74.8
Ti-YNU-1-249[b]	249	520.4	69.3	93.2	6.8	79.4
Ti-YNU-1-227[b]	227	511.0	74.6	91.8	8.2	67.5
Ti-YNU-1-155[c]	155	362.5	77.3	91.7	8.3	68.9
Ti-Beta-44	44	43.0	31.6	51.7	43.3	41.8
Ti-Beta-31	31	63.2	65.2	78.0	22.0	58.8

[a] Reaction conditions: 60 °C, 4 h, 0.1 g catalyst, 5 mL MeCN, 5 mmol substrate, 7.5 mmol H_2O_2 (31% in aqueous solution).
[b] Acid-treatment conditions: *L*/*S* = 100.
[c] *L*/*S* = 40.
[d] H_2O_2 efficiency.

catalysis of various alkenes; and (3) epoxidation of substituted alkenes and α,β-unsaturated ketones.

2. Experimental

2.1. Synthesis and characterization of samples

Ti-YNU-1 samples were post-synthesized according to the procedures reported in Ref. [15]. The Si/Ti ratio in the synthesis gel was in the range of 85–120. The as-synthesized samples were reflux-treated with 2 M HNO_3 aqueous solution (the liquid to solid (*L*/*S*) ratio varied from 30 to 100 (mL/g)) for 20 h before calcination. Ti-Beta was synthesized with a seeding method [6].

The XRD patterns (XRD) were recorded on a Mac Science M3X 1030 X-ray diffractometer with CuKα radiation. The diffuse reflectance (DR) UV–vis spectra of Ti-YNU-1 samples were measured on a Jasco V-550 UV-vis spectrophotometer. The adsorption of 1-hexene and 2-hexene on Ti-YNU-1 and Ti-Beta was measured at 25 °C on a Belsorp-Max high precision gas/vapor adsorption apparatus.

2.2. Catalytic measurements

The oxidation of various substrates was carried out at 0–75 °C for 0.17–4 h under stirring conditions in a 20 mL round-bottom flask immersed in a thermostatted water bath and equipped with a condenser. In a typical batch, 0.1 g of catalyst, 5 mL of solvent, 5 mmol of alkene and 5 mmol of H_2O_2 (31% in aqueous solution) were employed. The reaction time was calculated from the time when the flask was immersed in the water bath. The product was analyzed by a Shimadzu GC-14A gas chromatograph equipped with a 50-m OV-1 capillary column and a flame ionization detector. The amount of the unconverted H_2O_2 was determined with 0.1 M $Ce(SO_4)_2$ aqueous solution by the titration method.

3. Results and discussion

3.1. Physicochemical properties of the prepared titanosilicates

XRD measurements show that all the prepared samples are highly crystalline single-phase Ti-Beta or Ti-YNU-1 with the exception that a mild acid treatment of lamellar Ti-MWW precursor before calcination led to formation of Ti-MWW in Ti-YNU-1, and the amount of Ti-MWW depends on the acid-treatment conditions, which will be shown in the following parts. DR UV-vis spectroscopy shows that all of Ti atoms in Ti-YNU-1 are tetrahedrally coordinated since only one band at 210 nm was observed (Fig. 1), whereas octahedrally coordinated Ti sites as well as tetrahedral Ti species are present in Ti-Beta, as evidenced by observing a shoulder band around 235 nm besides the band at about 215 nm.

3.2. Influences of catalytic conditions

3.2.1. Effect of Ti content

The previous studies showed that acetonitrile should be the solvent of choice considering both activity and selectivity if Ti-YNU-1 and Ti-Beta were used for the epoxidation of alkenes [15–18]. Hence, herein in all reactions acetonitrile was employed as a solvent. Table 1 gives the sample notations of Ti-YNU-1-*x* and Ti-Beta-*x* with *x* representing the Si/Ti ratio in the sample, and their catalytic results for the epoxidation of cycloheptene. As expected, the conversion increased with increasing Ti content for both materials. It is noteworthy that Ti-YNU-1 not only showed higher activity but also gave much higher epoxide selectivity than Ti-Beta. However, attempt to further increase the Ti content in Ti-YNU-1 led to the formation of Ti-MWW structure, and the higher the Ti content in the sample, the more the formed Ti-MWW [16]. The 10-MR pore openings of Ti-MWW hinder bulky cycloheptene molecules from diffusing into the channels and accessing Ti sites, consequently resulting in a reduction in the activity with increasing Ti content in the sample, as evidenced by the decrease in the TON. Table 1 also shows that H_2O_2 efficiency over Ti-YNU-1 is superior to that over Ti-Beta. This may result from the fact that a significant amount of acid sites, originating numerous defect sites, are present in Ti-Beta [17].

3.2.2. Effect of H_2O_2/cycloheptene ratio

As is shown in Table 2, the H_2O_2/cycloheptene ratio has no strong influence on the catalytic performance of Ti-YNU-1-227 in the oxidation of cycloheptene within the experimental range. Of course, the H_2O_2 amount could not be too small (H_2O_2/cycloheptene < 0.75 in theory); otherwise, the complete

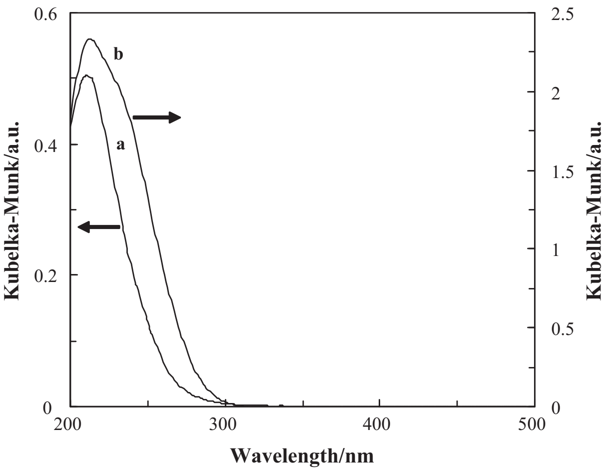


Fig. 1. DR UV–vis spectra of Ti-YNU-1-227 (a) and Ti-Beta (b).

Table 2
Catalytic results of Ti-YNU-1-227 in the epoxidation of cycloheptene at different H_2O_2/c-C_7H_{12} ratios[a].

Samples	H_2O_2/c-C_7H_{12}	Conv. (%)	Selectivity (%)		H_2O_2 eff. (%)[b]
			Epoxide	Others	
Ti-YNU-1-227	1	71.2	92.6	7.4	79.7
Ti-YNU-1-227	1.5	74.6	91.8	7.2	66.8
Ti-YNU-1-227	2	75.8	91.5	8.5	65.0

[a] Reaction conditions: 60 °C, 4 h, 0.1 g catalyst, 5 mmol substrate, 5–10 mmol H_2O_2 (31% in aqueous solution), 5 mL MeCN.
[b] H_2O_2 efficiency.

consumption of the oxidant would prevent the progress of the reaction.

3.2.3. Effect of acid treatment

It is known that the acid treatment of Ti-MWW before calcination is necessary for obtaining high activity and selectivity in the epoxidation of alkenes. Particularly, this process is indispensable for the formation of Ti-YNU-1 [15,16]. Thus, it is reasonable to deduce that the acid-treatment conditions would have a strong effect on the catalytic performance of Ti-YNU-1. Indeed, it was found that the optimum liquid/solid (*L*/*S*) ratio should be between 40 and 50 mL/g in terms of cycloheptene conversion if the sample was treated with 2 M HNO_3 for 20 h under reflux conditions (Fig. 2A). When the *L*/*S* ratio was too low, i.e. 30, the prepared sample contained less Ti-YNU-1 (Fig. 2B). However, when Ti-MWW precursor was subjected to heavy treatment with acid (the *L*/*S* ratio > 70), a large amount of Ti species were washed away, thus decreasing the active sites and lowering the conversion.

3.2.4. Effect of reaction temperature

The epoxidation of cycloheptene over Ti-YNU-1-267 is greatly dependent on the reaction temperature and comparable with that over Ti-Beta (Fig. 3). Cycloheptene conversion almost linearly increased with the temperature for both materials, while the reverse trend was observed for epoxide selectivity. Nevertheless, Ti-YNU-1-267 gave a very high selectivity, which was maintained above 90% regardless of the reaction temperature, whereas the epoxide selectivity on Ti-Beta-44 declined to 78% when the temperature was increased to 75 °C. In addition, Fig. 3 shows that the reaction temperature has a significant influence also on the H_2O_2 efficiency. The highest H_2O_2 efficiency for both materials was obtained at the same temperature of 40 °C. This can be explained as follows: H_2O_2 was consumed via two routes. One was for the oxidation of substrates; the other was consumed by thermal decomposition. Generally, high conversion gives high H_2O_2 efficiency [17,18]. Therefore, it is reasonable of the observance that H_2O_2 efficiency increases with increasing reaction temperature below 40 °C because of the marked increase in cycloheptene conversion. However, at high reaction temperature, decomposition of H_2O_2 becomes appreciable, and the degree increased with increasing reaction temperature as a result of higher activation energy for decomposition of H_2O_2 than for formation of epoxide through the attack of active oxygen species by the π electrons of alkenes. Therefore, the H_2O_2 efficiency conversely decreased when the reaction temperature was higher than 40 °C.

3.2.5. Effect of reaction time

Fig. 4 shows the catalytic results of Ti-YNU-1-155 and Ti-Beta-44 for the oxidation of cycloheptene as a function of reaction time. It is clear that cycloheptene conversion quickly increased to about 71% and 59% within 1.5 h over the Ti-YNU-1-155 and Ti-Beta-44, respectively. Then, a plateau was observed, especially while the reaction time was longer than 2.5 h. Nevertheless, Ti-YNU-1-155 exhibited higher conversion than Ti-Beta-44 and the difference became more marked with increasing reaction time. The gradual reduction of reaction rate is due to the consumption of the substrate, resulting in a decrease in the substrate content, and the deposition of large-molecule organic compounds in the channels [19]. In addition, it can be seen that cycloheptene conversion over the Ti-YNU-1-155 could reach as high as 41% at the reaction time of 10 min, implying the very fast initial reaction rate. The high selectivity (>90%) of Ti-YNU-1-155 indicates that the ring opening of cycloheptene oxide is not severe, but this side reaction occurs much more seriously over the Ti-Beta-44 owing to the presence of weak acid sites [11,17]. Although H_2O_2 efficiency decreased as the reaction time increased for both materials, it was higher on the Ti-YNU-1-155 than on the Ti-Beta-44.

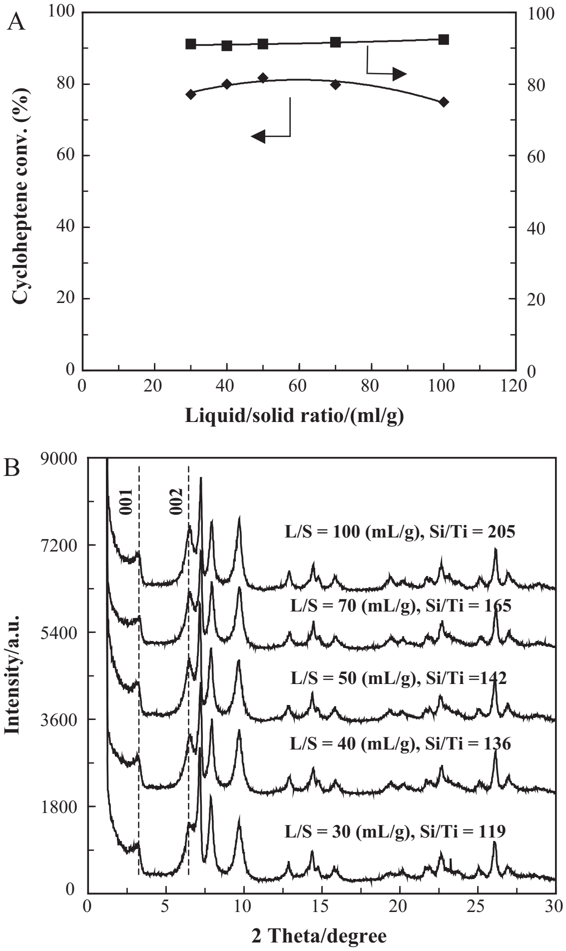


Fig. 2. Catalytic results (A) and XRD patterns (B) of the Ti-YNU-1 prepared by treating the postsynthesized Ti-MWW lamellar precursor with different amounts of 2 M HNO_3 aqueous solution for 20 h before calcination (reaction conditions: 60 °C, 2.5 h, 0.1 g catalyst, 5 mL MeCN, 5 mmol substrate, 7.5 mmol H_2O_2 (31% in aqueous solution)).

3.2.6. Effect of catalyst amount

The above studies show that Ti-YNU-1 is a potential, environmentally benign heterogeneous catalyst for the epoxidation of cycloheptene. With regard to the activity, epoxide selectivity and H_2O_2 efficiency, Ti-YNU-1 is highly superior to Ti-Beta. In particular, the catalytic stability of the former is also much better than that of the latter [16]. After 8 repeated runs, the structure of Ti-YNU-1 and the tetrahedral coordination state of Ti species were kept, while the irreversible change of the Ti state from the tetrahedral to octahedral coordination occurred to Ti-Beta [16]. Nevertheless, the

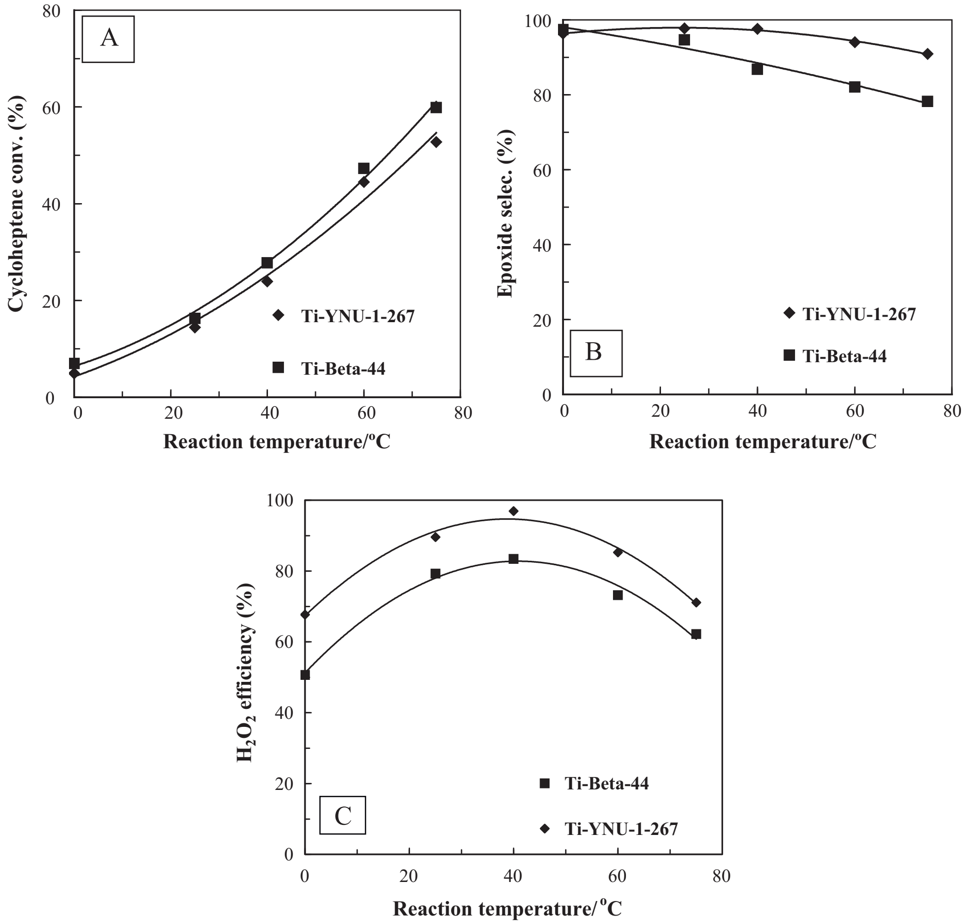


Fig. 3. Dependence of (A) cycloheptene conversion, (B) cycloheptene oxide selectivity and (C) H_2O_2 efficiency on the reaction temperature (reaction conditions: 1 h, 0.1 g catalyst, 5 mL MeCN, 5 mmol substrate, 7.5 mmol H_2O_2 (31% in aqueous solution)).

influence of the relative amount of Ti-YNU-1 to the substrate on its catalytic performance is still an issue. Fig. 5 illustrates the effects and makes the comparison with Ti-Beta. As expected, the cycloheptene conversion monotonically increased with the catalyst amount for both the Ti-YNU-1-155 and Ti-Beta-44. However, the epoxide selectivity of Ti-Beta-44 sharply reduced while that of Ti-YNU-1-155 was almost constant. As a result, the more the catalyst was used, the higher the epoxide yield was obtained over Ti-YNU-1-155 than on Ti-Beta-44. This arises from the presence of more acid sites in the oxidation system when more Ti-Beta-44 was used, resulting in the more severe hydrolysis of the once formed epoxide. In contrast, this problem was not serious for Ti-YNU-1-155, indicating that its hydrolysis acidity is negligible. This is favorable for the selective formation of epoxides and suppressing the occurrence of acid-induced side reactions.

3.3. Shape-selective catalytic properties of Ti-YNU-1 and Ti-Beta in the oxidation of alkenes

One of the unique features of molecular sieves is their shape-selective catalysis, which is very important in chemical industry. Fig. 6 compares the results of Ti-YNU-1-249 for the competitive oxidation of cycloheptene and other linear or cycloalkenes with those of Ti-Beta-44. The ratio of cycloheptene to other substrates was maintained at the level of 3/2 (mmol/mmol). Regardless of the titanosilicates used, the presence of other alkenes led to a decrease in cycloheptene conversion. With respect to 1-hexene, 2-hexene and cyclopentene, the cycloheptene conversion just slightly declined for both the Ti-YNU-1-249 and the Ti-Beta-44. This indicates that the presence of these three types of alkenes does not heavily affect the diffusion of cycloheptene into the channels of Ti-YNU-1-249 and Ti-Beta-44 [20], since the smaller the substrate molecule is, the easier the diffusion is. In contrast, in the case of 1-methylcyclopentene and especially cyclohexene, cycloheptene conversion significantly lowered down although it was not so evident over the Ti-Beta-44 as that over the Ti-YNU-1-249. This implies that the presence of C_6 cycloalkenes exerts a severe adverse effect on the cycloheptene diffusion and/or adsorption. Although the addition of cyclooctene to the reaction mixture had no influence on the conversion of cycloheptene over the Ti-YNU-1-249, it led to a drastic reduction in the cycloheptene conversion on the Ti-Beta-44. This is partially due to the slightly smaller pore opening of Ti-YNU-1-249 than that of Ti-Beta-44 [15,16], which makes cyclooctene molecules hard to diffuse into the pores of Ti-YNU-1-249. The difference observed in the epoxidation of single olefin and two types of alkenes suggests that the activity and selectivity of titanosilicates for the epoxidation of alkenes could be controlled by addition of another type of alkene.

Here it is worth noting that Ti-Beta-44 showed much higher conversion for 1-hexene than for 2-hexene in the presence of cycloheptene. Considering the electronic effect, 2-hexene would be more reactive. Indeed, it was found that the conversions of 1-hexene on Ti-Beta-44 without cycloheptene were 18.0% under the similar reaction conditions, whereas that of 2-hexene were 35.9%. Such contradictory results probably arise from the unique structure of Ti-Beta-44, and two types of steric effects may exert on the epoxidation of alkenes. One is the diffusion of alkene molecules, the other is the coordination behavior of alkene molecule to active Ti

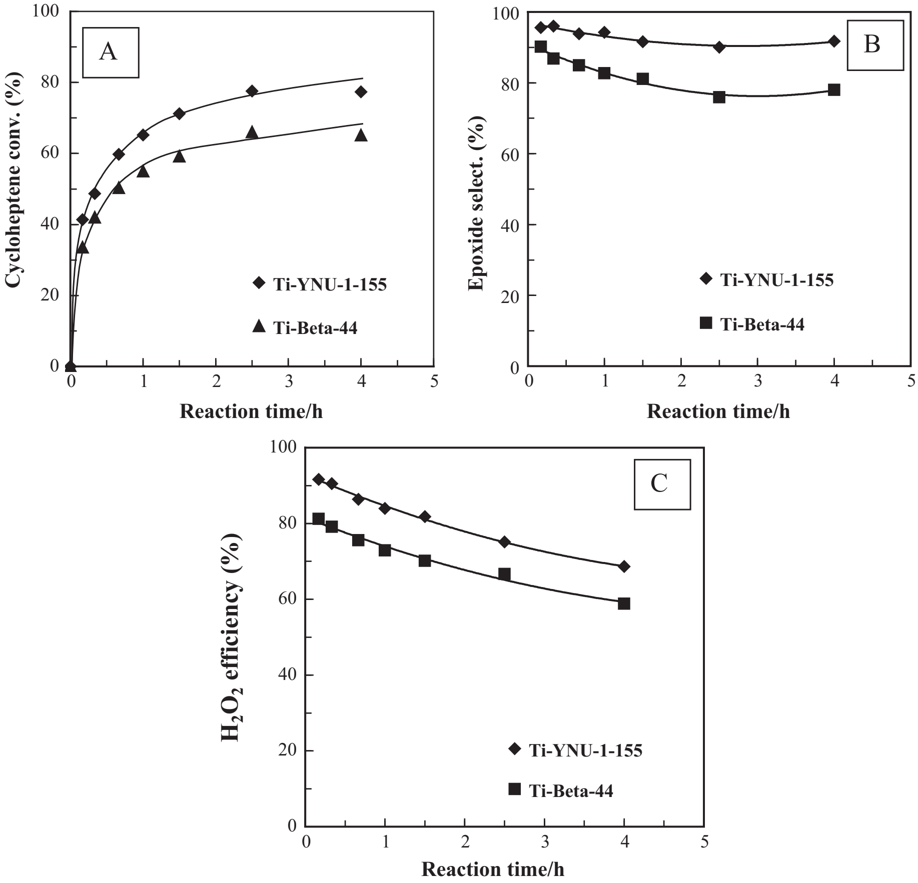


Fig. 4. Dependence of (A) cycloheptene conversion, (B) cycloheptene oxide selectivity and (C) H_2O_2 efficiency on the reaction time (reaction conditions: 60 °C, 0.1 g catalyst, 5 mL MeCN, 5 mmol substrate, 7.5 mmol H_2O_2 (31% in aqueous solution)).

species. Fig. 7 shows the adsorption isotherms of 1-hexene and 2-hexene on Ti-YNU-1-249 and Ti-Beta-44 at 25 °C. It is unexpected that these two titanosilicates showed a converse adsorption behavior. Ti-YNU-1-249 exhibited a higher capacity for 1-hexene than for 2-hexene, whereas Ti-Beta-44 gave a much faster adsorption rate for 2-hexene than for 1-hexene. If the diffusion of alkene molecule is the predominant reason, Ti-YNU-1-249 would show higher activity for 1-hexene than for 2-hexene, while Ti-Beta-44 would give a higher conversion of 2-hexene than of 1-hexene. Although this is true for Ti-Beta-44 in the absence of cycloheptene, it is contrary to the results obtained over the Ti-Beta-44 in the presence of cycloheptene and over the Ti-YNU-1-249. This shows that both the electronic characters and the coordination behaviors of 1-hexene and 2-hexene molecules might play a very important role in the epoxidation of these two alkenes on the Ti-YNU-1-249 and the Ti-Beta-44 in the presence of cycloheptene. This is also confirmed by the results obtained in the absence of cycloheptene that a higher conversion was obtained for 2-hexene than for 1-hexene irrespective of the titanosilicates, showing that the electronic effect could prevail over the geometric effect in total since both 1-hexene and 2-hexene can be epoxidized in the intralayer and interlayer channels of Ti-YNU-1-249.

Ti-Beta has a pore size of 7.1 × 7.3 Å, indicating a nearly round pore-opening. Similarly, cycloheptene is also almost a circular molecule with a dimension slightly smaller than the pore mouth of Ti-Beta; therefore, cycloheptene molecule would impose more constraints on the epoxidation of 2-hexene than of 1-hexene after interacting with five-coordinated Ti species [17,21,22]. 1-Hexene with less steric constraint might be able to easily access to and interact with the active Ti sites, whereas this was somehow hindered for 2-hexene because the coordination complex molecular size of 2-hexene is larger than that of 1-hexene (Scheme 1), resulting in a lower conversion of 2-hexene than of 1-hexene. Nevertheless, with respect to Ti-YNU-1, the difference originating from the coordination restriction between 1-hexene and 2-hexene would be much smaller than Ti-Beta as a result of having an independent intralayer sinusoidal channel with a 10-MR pore-opening in Ti-YNU-1, which does not allow the diffusion of cycloheptene molecules but linear alkenes into the intralayer space. Thus, the intralayer sinusoidal channel would only allow the epoxidation of 1-hexene or 2-hexene, and cycloheptene can only be epoxidized in the interlayer void space with 12-MR pore-openings. It was reported that Ti-MWW preferentially catalyzes the epoxidation of *trans* 2-hexene [23]. This also held true for Ti-YNU-1, which has the same intralayer structure as Ti-MWW but an expanded interlayer space. A *trans*-epoxide/*cis*-one molar ratio of 5.24 was obtained over the Ti-YNU-1-249 for the epoxidation of 2-hexene with a *trans*-isomer/*cis*-isomer molar ratio of 1.36. When a certain amount of cycloheptene (cycloheptene/2-hexene = 3/2) was added to the reaction mixture, much more *trans*-2-hexene epoxide (*trans*-isomer/*cis*-one = 4.21) was still formed. In contrast, Ti-Beta-44 showed a *trans*-epoxide/*cis*-one molar ratio of 0.45 and 0.56 in the absence and the presence of cycloheptene respectively under the same reaction conditions because the *cis*-2-hexene is more reactive than the *trans*-isomer.

It seems that compared with cycloheptene, the bulkier cycloalkenes would show higher reactivity if there was no steric constraint probably because the bulkier cycloalkenes are more electron-rich. This is proved by the results of competitive oxidation of cycloheptene and cyclooctene over the Ti-Beta-44. The conver-

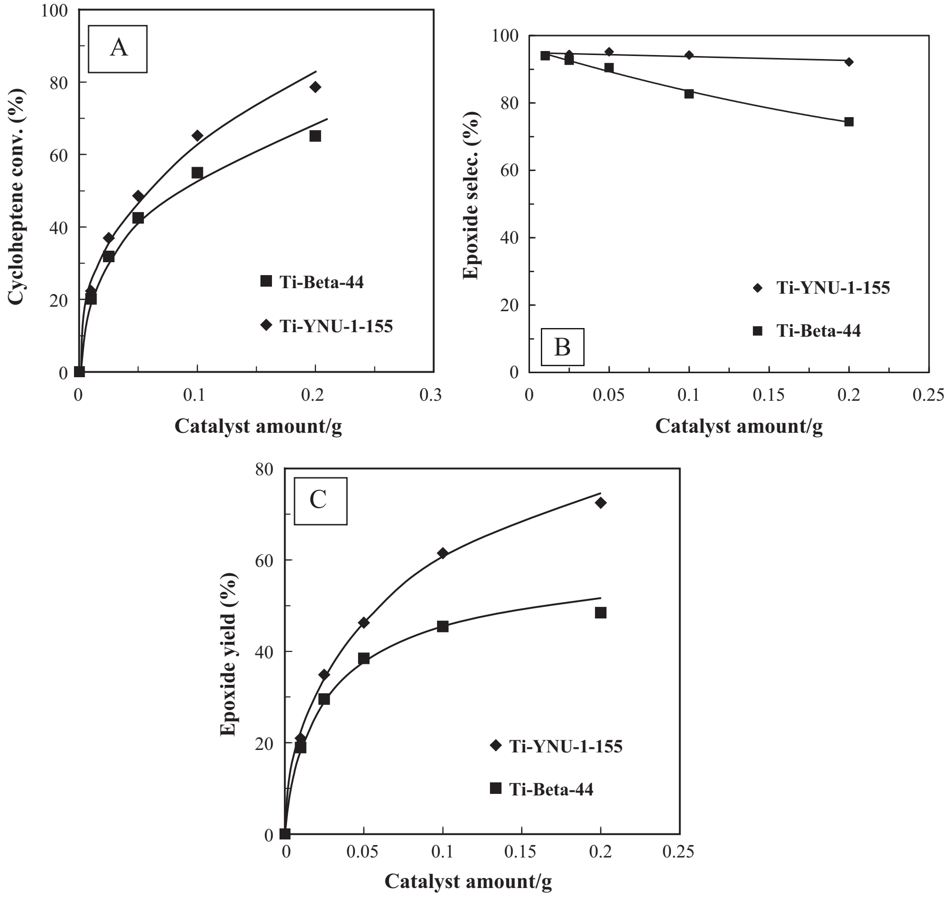
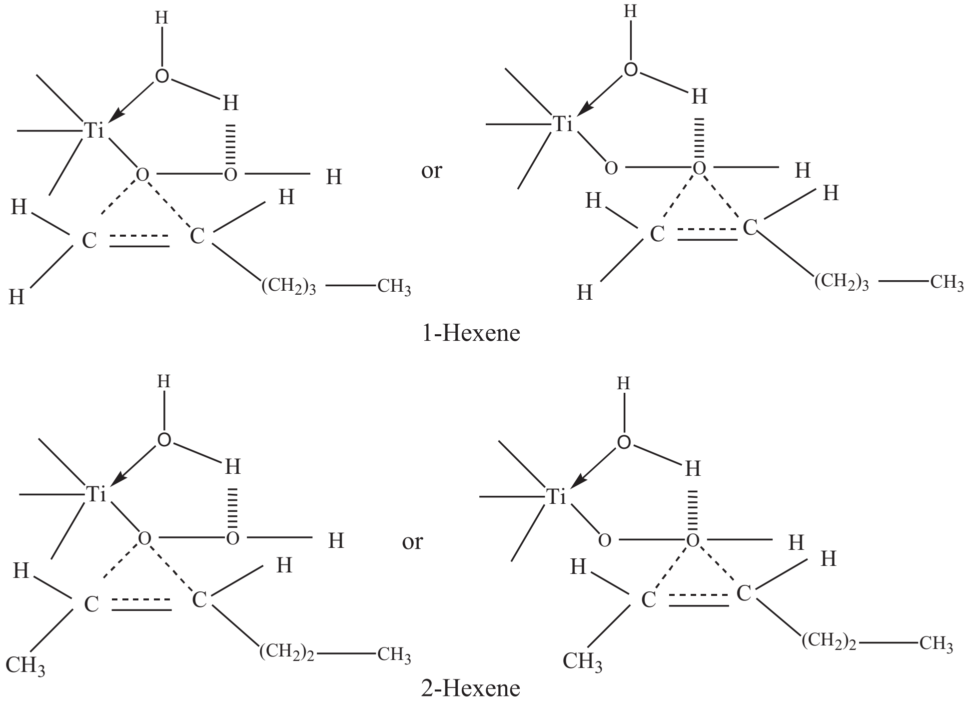


Fig. 5. Dependence of (A) cycloheptene conversion, (B) cycloheptene oxide selectivity and (C) cycloheptene oxide yield on the catalyst amount (reaction conditions: 1 h, 5 mL MeCN, 5 mmol substrate, 7.5 mmol H_2O_2 (31% in aqueous solution)).



Scheme 1. Plausible transition states of Ti-YNU-1 and Ti-Beta for catalyzing 1 hexene and 2-hexene molecules.

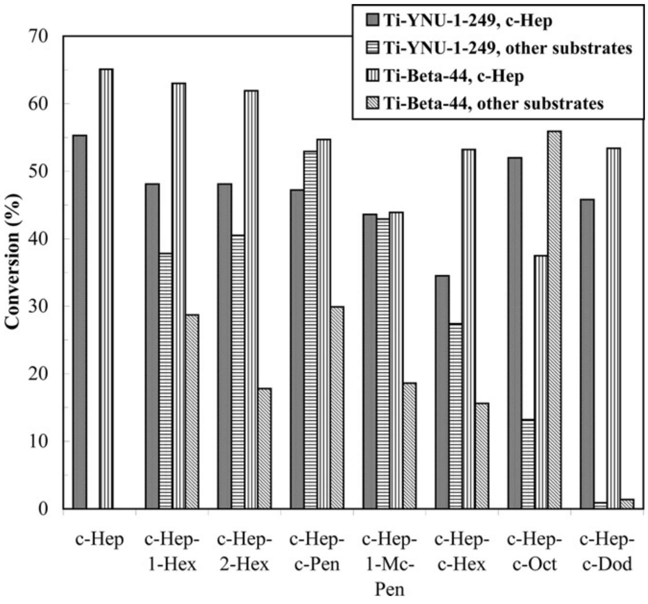


Fig. 6. Competitive oxidation of cycloheptene and other alkenes over Ti-YNU-1 and Ti-Beta ((1) c-Hep: cycloheptene; 1-Hex: 1-hexene; 2-Hex: 2-hexene; c-Pen: cyclopentene; 1-Mc-Pen: 1-methylcyclopentene; c-Hex: cyclohexene; c-Oct: cyclooctene; c-Dod: cyclododecene. (2) Reaction conditions: 60 °C, 1 h, 0.1 g catalyst, 5 mL MeCN, 3 mmol cycloheptene and 2 mmol other alkenes, 7.5 mmol H_2O_2 (31% in aqueous solution)).

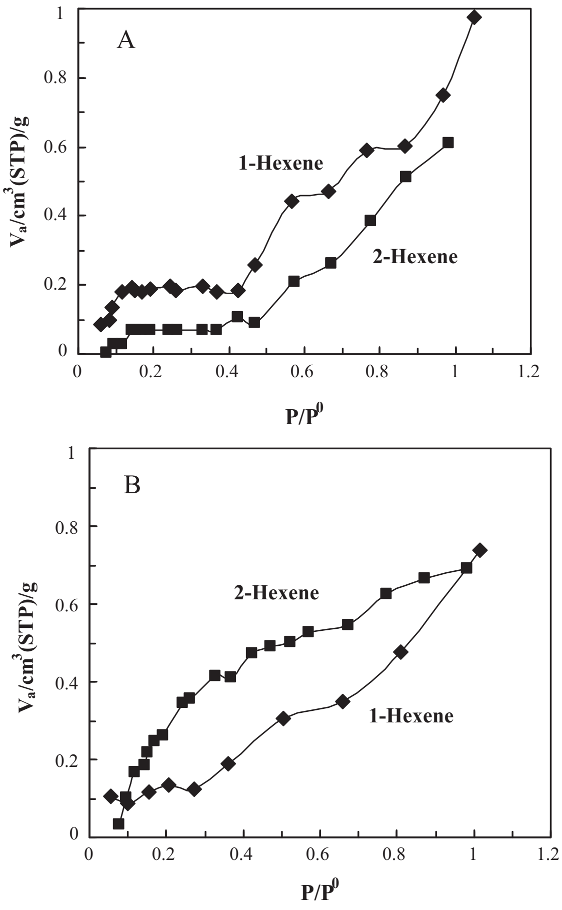


Fig. 7. Adsorption isotherms of 1-hexene and 2-hexene on Ti-YNU-1-249 (A) and Ti-Beta-44 (B) at 25 °C.

sion of cyclooctene obtained over Ti-Beta with a 12-MR ring pore opening corresponding to the bulkiness of cyclooctene was higher than that of cycloheptene [15]. Nevertheless, the steric effect is also a key factor to determine the activity. The much larger molecular size of cyclododecene than the pore openings of both the titanosilicates resulted in a quite low conversion. The presence of cyclodocene also led to a reduction in the cycloheptene conversion by about 17% for the two titanosilicates probably as a result of its partial blockage to the pore openings after coordinating to Ti intermediates on the external surface or at the pore mouth.

It is also evident in Fig. 6 that compared with Ti-Beta, Ti-YNU-1 were more active in the oxidation of cycloalkenes except for cyclooctene and cyclododecene. As a matter of fact, Ti-YNU-1 with high Ti content also gave higher conversion than Ti-Beta for the epoxidation of linear alkenes such as 1-hexene and 2-hexene. Ti-YNU-1-155 showed conversions of 35.5% and 54.1% for 1-hexene and 2-hexene respectively, both of which were higher than those of Ti-Beta-44. Also, Ti-YNU-1-155, like Ti-MWW, selectively catalyzed epoxidation of *trans*-2-hexene, while Ti-Beta favorably promoted the epoxidation of *cis*-isomers, as shown above. These findings show that Ti-YNU-1 is a unique titanosilicate catalyst for the epoxidation of various alkenes.

3.4. Epoxidation of substituted alkenes and α,β-unsaturated ketones

Epoxidation of substituted alkenes is widely used in fine chemical industry. This can be successfully achieved with peracids as oxidants, e.g. peracetic acid and *m*-chlorobenzoic acid [2]. However, this is not an environmentally friendly method as equivalent amounts of waste acid are produced. In addition, the safety issue associated with handling peracids is also a matter of concern. Therefore, there is a strong need to develop a heterogeneous catalyst that could employ clean oxidants such as O_2 and H_2O_2 to epoxidize alkenes and their derivatives.

Since the above investigations show that Ti-YNU-1 has a potential for the epoxidation of various linear and cycloalkenes, it is expected that Ti-YNU-1 would efficiently catalyze the oxidation of substituted alkenes. Indeed, compared with Ti-Beta-44, Ti-YNU-1-235 not only exhibited higher activity but also gave much higher epoxide selectivity and H_2O_2 efficiency for the studied substrates (Fig. 8A and B). In particular, the conversion of cyclopentene and 1-methylcyclopentene over Ti-YNU-1-235 reached about 90% although the epoxide selectivity was moderate. As far as cyclohexene and its substituted derivatives are concerned, Ti-YNU-1-235 owed a moderate activity but high epoxidation selectivity except for the oxidation of 1-methylcyclohexene. The epoxide selectivity can be further considerably increased by increasing relative amounts of substrates to the catalyst. It was found that the selectivity of cyclohexene oxide reached about 90% when the weight ratio of the substrate to the catalyst was increased from about 4.2 to 16.6. It is known that the rate of solvolysis depends on the structure of the epoxide formed in the first step [8]. When the methyl group is located at the position far from double bond, the rate of hydrolysis is slow, resulting in the high epoxide selectivity. However, if methyl group is present on the olefinic double bond, it would make the ring opening very quickly as a result of the facile ring-opening generating a tertiary carbenium cation followed by the nucleophilic attack to the cation according to the SN1 mechanism. This is prominent particularly for cyclopentene and cyclohexene derivatives. In these two cases, the epoxide must be in the form of "boat" cyclopentane or cyclohexane ring conformations [8], which are more reactive owing to its high strain, and thus, resulting in the rapid hydrolysis.

The conversion of 4-methylcyclohexene over Ti-YNU-1-235 slightly decreased by 5%, compared to cyclohexene, indicating that

Table 3
Catalytic results for the epoxidation of various unsaturated ketones over Ti-YNU-1-235 (Si/Ti = 235) and Ti-Beta-44 (Si/Ti = 44)[a].

Substrates	Ti-YNU-1-235				Ti-Beta (B)			
	Conv. (%)	Selec. (%)	TON	H_2O_2 eff. (%)[b]	Conv. (%)	Selec. (%)	TON	H_2O_2 eff. (%)[b]
2-Cyclopenten-1-one	13.3	100	94.3	48.8	44.5	100	60.5	58.2
2-Cyclohexen-1-one	57.9	99.3	410.5	85.2	73.5	98.7	100.0	84.9
3-Methyl-2-cyclopenten-1-one	n.d.	–	–	–	n.d.	–	–	–
3-Methyl-2-cyclohexen-1-one	n.d	–	–	–	6.9	68.8	9.4	–

[a] Reaction conditions: 60 °C, 2 h, 0.1 g catalyst, 5 mL MeCN, 5 mmol substrate, 5 mmol H_2O_2 (31% in aqueous solution).

[b] H_2O_2 efficiency.

the steric hindrance somewhat occurred. In contrast, this phenomenon was not observed for Ti-Beta-44. This further proves that the pore opening of Ti-YNU-1 is slightly smaller than that Ti-Beta.

The α,β-epoxy ketones are important raw materials for preparing α-hydroxy and β-hydroxy ketones by reductive cleavage. These materials are constituents or intermediates in perfume and flavorful substances, taxol, biologically active antitumor agents [1,24]. Thus, it is interesting to investigate the catalytic performance of Ti-YNU-1 for the epoxidation of α,β-unsaturated ketones. Table 3 lists the catalytic results of Ti-YNU-1-235 and Ti-Beta-44 for the oxidation of different carbonyl compounds. It is clear that Ti-Beta-44 showed high conversion than Ti-YNU-1-235 although its TON is lower. This seems to suggest that Ti-YNU-1 is highly active for the epoxidation of alkenes and their electron-rich derivatives, while Ti-Beta is appropriate for the oxidation of relatively electron-deficient α,β-unsaturated ketones possibly owing to the different crystalline structure. Ti-YNU-1 had a smaller pore-opening than Ti-Beta [15,16], and thus, more severe steric effect would be imposed on Ti-YNU-1 in the oxidation of α,β-cycloalkene ketones. Much higher activity of Ti-YNU-1 than of Ti-Beta in the epoxidation of alkenes indicates that the active oxygen species of Ti-YNU-1 might be more electronphilic than that of Ti-Beta, resulting in a lower conversion of α,β-unsaturated ketones obtained on the Ti-YNU-1-235. Nevertheless, while Ti-Beta-44 served as a catalyst, serious leaching of Ti species out of the framework occurred, and became more severe with increasing carbon number of these ketones perhaps due to actions of H_2O_2 and the formed large-molecule polyols [1,25,26]. This is evidenced by the fact that the color of the reaction mixture changed into bright yellow after the removal of catalyst, which is attributed to the soluble Ti species. The instability of Ti species in Ti-Beta-44 restricts its reusability. In contrast, Ti atoms in the framework of Ti-YNU-1-235 can stand against leaching during the reaction, as verified by the colorless liquid obtained after reaction. This shows that Ti-YNU-1 is a very stable titanosilicate and can be recycled for use. The moderate conversion of 2-cyclohexen-1-one over the Ti-YNU-1-235 shows that Ti-YNU-1 has the potentiality to act as a catalyst in the epoxidation of α,β-unsaturated ketones, at least of 2-cyclohexen-1-one. The lower reactivity of the five-membered ring ketones than that of the six-membered ring ones is in agreement with earlier reports [1,27,28]. This may be due to the resonance interaction between the C=C double bond and the electron-withdrawing C=O groups. In the case of 2-cyclopenten-1-one and its derivatives, the co-planarity of the atoms in the C=C–C=O system leads to electron deficiency of the C=C double bond, and hence lowering the reactivity. However, for 2-cyclohexen-1-one, the preferential conformation would make unfavorable the presence of the atoms of the C=C–C=O system in the same plane. As a result, the effective overlap of the four π-orbitals cannot be formed. Thus, the C=C double bond in this substrate is similar to an isolated C=C double bond, and consequently showing a high reactivity. Compared with 2-cyclohexen-1-one, the drastic reduction in the reactivity of 3-methyl-2-cyclohexen-1-one for both the Ti-YNU-1-235 and Ti-Beta-44 suggests that steric strain of the product should be another factor. Thus, it could be deduced that both the steric effect and the electron deficiency play an important role in the epoxidation of α,β-unsaturated ketones over titanosilicates.

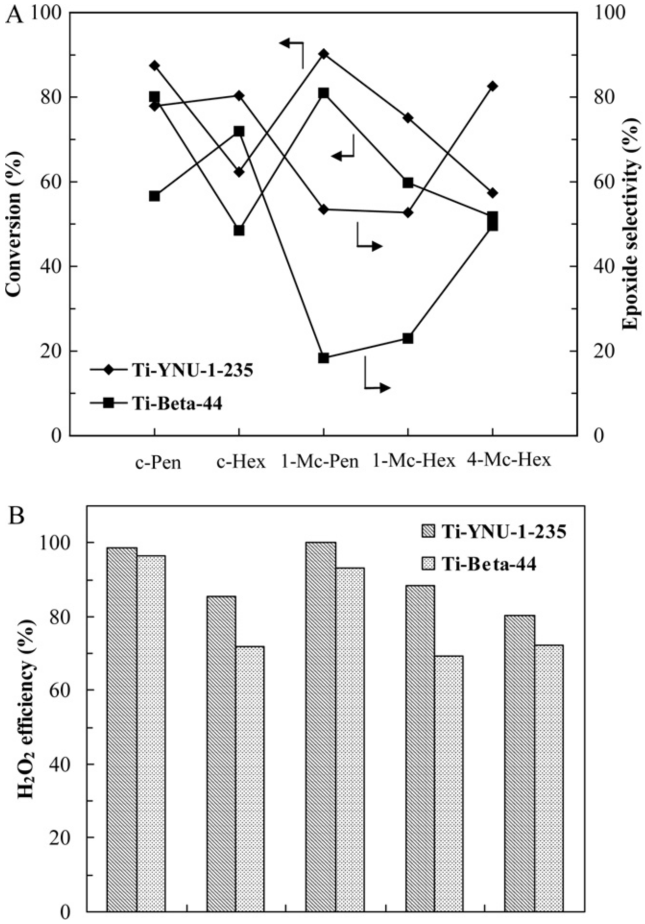


Fig. 8. Catalytic results of Ti-YNU-1-235 (Si/Ti = 235) and Ti-Beta-44 for the oxidation of cyclopentene, cyclohexene and their methyl-substituted derivatives (A) substrate conversion, and epoxide selectivity and (B) H_2O_2 efficiency ((1) c-Pen: cyclopentene; 1-Mc-Pen: 1-methylcyclopentene; c-Hex: cyclohexene; 1-Mc-Hex: 1-methylcyclohexene; 4-Mc-Hex: 4-methylcyclohexene. (2) Reaction conditions: 60 °C, 2 h, 0.1 g catalyst, 5 mL MeCN, 5 mmol substrate, 7.5 mmol H_2O_2 (31% in aqueous solution)).

4. Conclusions

Ti-YNU-1 can catalyze the epoxidation of alkenes and their electron-rich substituted derivatives with aqueous H_2O_2 solution more effectively and selectively than Ti-Beta. In addition, it also shows a higher H_2O_2 efficiency. Although it gives low conversion than Ti-Beta in the oxidation of α,β-unsaturated carbonyl compounds, it shows much higher stability. This evidences that

Ti-YNU-1 is an environmentally benign catalyst. The catalytic conditions have a strong influence on the catalytic performance of Ti-YNU-1 and Ti-Beta. Addition of 1-hexene, 2-hexene or cyclopentene into the reaction mixture does not heavily affect the conversion of cycloheptene over the Ti-YNU-1 and the Ti-Beta, but the presence of 1-methylcyclopentene and cyclohexene greatly decreases the activity of cycloheptene. Nevertheless, compared with Ti-Beta, Ti-YNU-1 is an intrinsically active and selective catalyst for the epoxidation of various alkenes, and also keeps the unique feature of Ti-MWW for the selective oxidation of *trans*-2-hexene.

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