Phase-Boundary Catalysis of Alkene Epoxidation with Aqueous Hydrogen Peroxide Using Amphiphilic Zeolite Particles Loaded with Titanium Oxide

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A new heterogeneous catalytic system, phase-boundary catalysis, for epoxidation of alkene with aqueous H_2O_2 is proposed. Amphiphilic titanium-loaded zeolite particles, a part of the external surface of which was covered with hydrophobic alkyl groups and the rest being left hydrophilic, were prepared by deposition of titanium species from titanium(IV) tetra-2-propoxide and attachment of octadecylsilyl groups from *n*-octadecyltrichlorosilane (ODS) onto an NaY zeolite powder. Due to their amphiphilicity, the catalyst particles lay at the liquid–liquid phase boundary between upper alkene and lower aqueous phases, and they showed catalytic activity for epoxidation of 1-alkenes (e.g., 1-octene) with aqueous hydrogen peroxide. The phase-boundary catalytic system required neither stirring to make an emulsion nor addition of a cosolvent to make a homogeneous solution to drive the epoxidation. The yield of 1,2-epoxyoctane, a sole oxidation product from 1-octene, strongly depended on the apparent interphase area of the aqueous–organic phase boundary. The amphiphilic catalyst exhibited much higher catalytic activity than that of hydrophilic titanium-loaded NaY, without modification by ODS, or of a hydrophobic catalyst with almost full coverage by the alkyl groups. A similar trend in the activities of these catalysts was also observed when the reaction was carried out with vigorous stirring, in the presence of a cosolvent, or in a water-carbontetrachloride (CCl_4) mixture, where the aqueous hydrogen peroxide phase lies above the CCl_4 phase. The phase-boundary catalytic system could also be applied to epoxidation of other normal alkenes. Compared with nonporous silica particles, the use of microporous NaY with a relatively large surface area had a beneficial effect, probably due to an increase both in the surface contact between the aqueous and organic layer and in the number of effective active sites of titanium species on its external surface. On the basis of these experimental results, a reaction model is proposed.   © 2001 Elsevier Science

Key Words: phase-boundary catalysis; amphiphilic zeolite particles; epoxidation; alkene; hydrogen peroxide; *n*-octadecyltrichlorosilane.

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INTRODUCTION

Due to increasing demand for clean and environmentally benign technologies in chemical process engineering, much attention has recently been paid to the establishment of ecologically more acceptable catalytic processes, including removal of toxic and expensive reagents, minimization of by-product formations, and simplification of workup procedures (1). In liquid-phase epoxidation of olefins, for example, various transition metal complexes are used as homogeneous catalysts because they show high selectivity and activity. However, substitution of these homogeneous catalytic systems with heterogeneous systems is desirable because of the simplicity of catalyst and product isolation from the reaction mixture and because of the possibility of operating the reaction continuously in heterogeneous systems.

In order to realize a cleaner oxidation process in the liquid phase, the selection of oxidants is important. Hydrogen peroxide (H_2O_2) is one of the most promising oxidants for a clean oxidation process because it gives only water as a product in a wide range of oxidation reactions. Moreover, it is less expensive and more accessible than other oxidizing agents, such as organic peracids or hydroperoxides. Therefore, heterogeneous catalytic oxidation using aqueous H_2O_2 would be desirable. However, one of the major problems encountered in this system is insufficient transfer of substrate and/or reagent molecules between organic solvent and water phases. The addition of cosolvents, leading to a homogeneous solution and eliminating the liquid–liquid phase boundaries, has been a general strategy (2, 3). Alternatively, the reaction rate could be improved by vigorous stirring to increase the apparent interface area (4). However, the presence of a third component or cosolvent or the formation of an emulsion by stirring would make the workup procedure very tedious.

Recently, we have proposed a new approach, called phase-boundary catalysis (PBC), for catalyzing the liquid–liquid phase reaction by using a solid catalyst and H_2O_2 under cosolvent-free conditions (5). The concept is based on the idea that an amphiphilic catalyst particle can be placed

at the liquid–liquid phase boundary in order to catalyze the reaction without the presence of a cosolvent and without the formation of an emulsion containing a catalyst by vigorous stirring. Actually, we have demonstrated that amphiphilic Ti-loaded NaY zeolite prepared by partial modification with alkylsilane successively catalyzes epoxidation of 1-octene in this system. To the best of our knowledge, no catalytic reactions in a solid catalyst–H_2O_2 system similar to the PBC concept have been reported up to now. Here, we show the details and the mechanism of PBC for alkene epoxidation.

EXPERIMENTAL

Catalyst Preparation

NaY zeolite (JRC-Z-Y5.5) powder was supplied as a reference catalyst from the Catalysis Society of Japan and used as obtained. Partially modified zeolite, whose external surface was partly covered with alkylsilane, was prepared in two steps. First, titanium(IV) tetra-2-propoxide ($Ti(OPr^i)_4$, Wako Pure Chemical) was impregnated from its benzene solution into NaY zeolite powder and heated at 383 K overnight. Here, this modified zeolite is called w-Ti–NaY. The molar amount of Ti was 500 μmol g^{-1} of NaY, unless otherwise stated. In the second step, the w-Ti–NaY powder with water (50 wt%) was immersed in 10 cm^3 toluene containing 500 μmol of n-octadecyltrichlorosilane (ODS, ShinEtsu), and the suspension was shaken for ca. 5 min at room temperature. Then, the solid was collected by centrifugation and dried at 383 K overnight. Due to the hydrophilicity of the w-Ti–NaY surface, the addition of a small amount of water led to aggregation by the capillary force of water among particles (6). Under these conditions, it is expected that only the outer surface of aggregates, being in contact with the organic phase, could be modified with ODS. The partially modified sample was labeled w-Ti–NaY. A similar procedure was also carried out for nonporous silica with a primary particle size of 500 nm (Nissan Chemical Industries), and it was labeled as w/o-Ti–silica.

Fully modified Ti–NaY (o-Ti–NaY) was prepared by a procedure similar to that reported previously (7). ODS (500 μmol) was dissolved in a mixed solution of toluene (80 vol%) and CCl$_4$ (20 vol%). A dried sample of w-Ti–NaY (1 g) was added to the solution, and the mixture was stirred overnight at room temperature. A solid sample was collected by centrifugation, washed with CCl$_4$ and then ethanol, and dried at 383 K overnight.

Amorphous titanium oxide (TiO_2) was also prepared according to the previously reported method (8) and modified with ODS. To a $Ti(OPr^i)_4$ 8 g ethanol (40 cm^3) solution, an ethanol (30 cm^3)–water mixture (30 cm^3) was added dropwise with vigorous stirring. White TiO_2 precipitate was dried at 383 K overnight. The TiO_2 sample was partially modified with ODS (w/o-Ti) by the same method as that used for the w/o-Ti–NaY preparation.

Reaction Conditions and Analytical Methods

Epoxidation of straight-chain alkenes such as 1-pentene, 1-hexene, 1-octene, and 1-dodecene was carried out under several reaction conditions. Typically, alkene (4 cm^3), 30% aqueous H_2O_2 (1 cm^3, Wako), and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with or without stirring for 20 h at room temperature. Except for 1-octene, all of the alkenes, purchased from Kanto Chemicals, were used as obtained. Because of the presence of an appreciable amount of impurities, 1-octene was purified by passing through a column of basic alumina (Merck). The reaction products were analyzed by gas chromatography (a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and PEG1000 and TENAX TA60/80 columns).

RESULTS AND DISCUSSION

Physical Properties

Figure 1 shows the apparent distribution of modified Ti–NaY catalysts suspended in an aqueous H_2O_2 (30%)–1-octene mixture. Since the original unmodified NaY and the loaded titanium oxide species are hydrophilic and do not easily disperse in organic solvents, the w-Ti–NaY was dispersed well in the aqueous phase, as expected (Fig. 1a). On the other hand, o-Ti–NaY was dispersed very well in the organic 1-octene phase due to its hydrophobic nature of covering octadecylsilyl groups on the external surface of Ti–NaY (Fig. 1c). It is worth noting that, compared with these modified NaY catalysts, almost all of the w/o-Ti–NaY particles were located at the aqueous–organic phase boundary (Fig. 1b). The characteristic behavior of w/o-Ti–NaY is attributable to its amphiphilicity (i.e., each w/o-Ti–NaY particle has both hydrophilic and hydrophobic faces).

In the water adsorption experiment, it was observed that the adsorption capacity of ODS-modified NaY catalysts at ambient temperature (8 mmol g^{-1} for both w/o-Ti–NaY and o-Ti–NaY) was not so different from that of the parent NaY zeolite (11 mmol g^{-1}), indicating that the structure and hydrophilic features of internal pores of these NaY particles were retained and that the hydrophobic alkyl chains did not block the entrance of zeolite pores. These results agree well with the findings reported by Singh and Dutta (7).

Catalytic Properties for Epoxidation of 1-Octene

Table 1 summarizes the yields of 1,2-epoxyoctane and turnover number (TON) per Ti atom in epoxidation of 1-octene with aqueous H_2O_2 by using several catalysts under the condition of stirring. All of the modified NaY catalysts
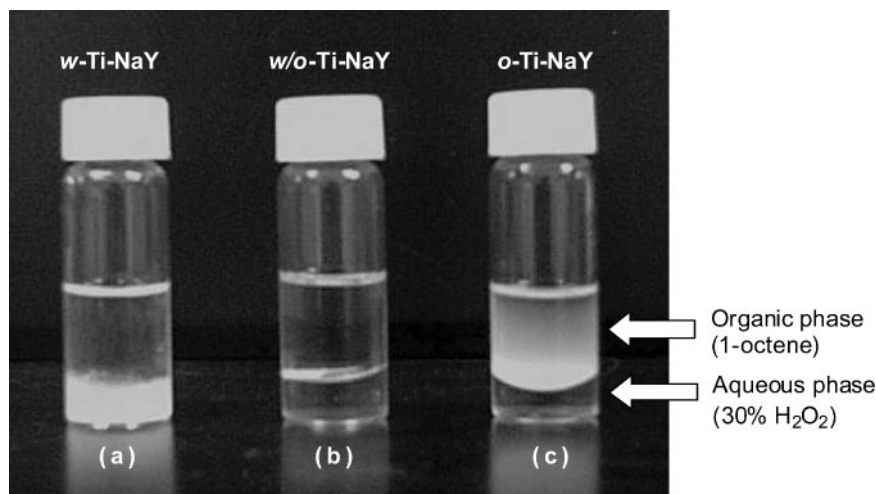
FIG. 1. Modified Ti–NaY zeolite in the mixture of aqueous and organic phases.

showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane (entries 2–4), and the reaction did not occur without catalysts (entry 1). Gas chromatography analyses indicated that 1,2-epoxyoctane was the sole product, and other expected by-products, such as 2-octanone, 1-octanol, 2-octanol, or 1,2-octanediol, were not detected. Modification of Ti–NaY with hydrophobic alkyl groups led to a significant rate enhancement. In particular, a partly modified catalyst (w/o-Ti–NaY, entry 3) showed much higher activity than did a fully modified one (o-Ti–NaY, entry 4) in the reaction at room temperature. A considerable increase in epoxide yield was also observed when the temperature was increased to 353 K using w/o-Ti–NaY as a catalyst (entry 5).

TABLE 1

Epoxidation of 1-Octene by Variously Modified NaY Zeolite[a]

Entry	Catalyst	Epoxide yield/μmol	TON for Ti
1	None	0.1	—
2	w-Ti–NaY	2.5	0.1
3	w/o-Ti–NaY	27.4	1.1
4	o-Ti–NaY	5.9	0.2
5	w/o-Ti–NaY[b]	88.7	3.6
6	w/o-Ti–NaY[c]	22.7	45.4
7	w/o-Ti–NaY reused[d]	16.4	0.7
8	Solution[e]	0.1	—
9	w/o-Ti	25.9	—
10	w/o-Ti reused[d]	6.0	—

[a] All reactions were carried out at room temperature for 20 h with 1-octene (4 cm^3), 30% H_2O_2 (1 cm^3), and catalyst (50 mg) with vigorous stirring. The concentration of Ti and alkylsilane was 500 μmol g^{-1}.

[b] The reaction temperature was 353 K with the catalyst of entry 3.

[c] The concentration of Ti was 10 μmol g^{-1}.

[d] The reaction was performed after the catalyst was washed with methanol and dried at 338 K for 4 h.

[e] The aqueous phase of entry 3 after the reaction. The reaction was conducted for 9 h.

The TON, the molar ratio of the epoxide to the loaded Ti, was almost unity for the reaction with w/o-Ti–NaY (entry 3) of relatively larger Ti loading. On the other hand, w/o-Ti–NaY with a lower Ti concentration (10 μmol g^{-1}, entry 6) gave a TON of ca. 45, indicating catalytic action of Ti species. The higher loading might induce aggregation to make inactive inner Ti species.

Although w/o-Ti–NaY showed higher catalytic activity in an aqueous–organic (W/O) mixture, it is not clear whether the observed reaction proceeds with Ti species loaded on NaY particles or with those leached in the reaction mixture. In order to exclude the latter possibility, the w/o-Ti–NaY catalyst recovered and dried after reaction for 20 h (entry 3) was reused in a fresh W/O mixture, and the remaining reaction mixture, without the catalyst, was vigorously stirred for 9 h with addition of 30% H_2O_2. The activity of recovered w/o-Ti–NaY was ca. 60% of that of the fresh w/o-Ti–NaY (entry 7), but a negligible increase in the molar amount of epoxide could be seen in the latter solution (entry 8). These facts suggest that the epoxidation was catalyzed by the w/o-Ti–NaY particles but not by the leached Ti species. A decrease in activity, similar to that seen in the recovered w/o-Ti–NaY, was observed when amorphous TiO_2 was modified with ODS (w/o-Ti) by a procedure similar to that used for the w/o-Ti–NaY preparation; the activities of the recovered and dried w/o-Ti were decreased to ca. 75% (entries 9 and 10). Therefore, the decrease in activity of recovered w/o-Ti–NaY was attributed to surface modification, such as detachment of the alkyl chains or modification of the titanium species, during the reaction and/or regeneration processes of the catalyst.

Phase-Boundary Catalysis

Figure 2 shows the effect of stirring on the yield of 1,2-epoxyoctane. The activity of w-Ti–NaY was appreciable
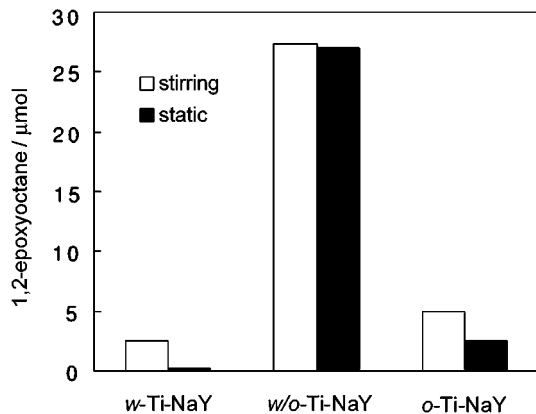
FIG. 2. The yield of 1,2-epoxyoctane using variously modified NaY under stirring and static conditions.

under the condition of vigorous stirring (i.e., in the W/O emulsion) but was negligible without stirring. Similar behavior was seen in the o-Ti–NaY system in which the epoxide yield under static conditions was almost half that of the stirred reaction mixture. On the other hand, the activity of w/o-Ti–NaY was independent of the stirring rate (i.e., this catalyst did not require the formation of a W/O emulsion by stirring). This is one of the most striking characteristics of w/o-Ti–NaY and is completely different from previously reported results for the cosolvent free "triphase system" (9–11).

Thus, when w/o-Ti–NaY was added to the W/O mixture, it spontaneously lay at the phase boundary (see Fig. 1) and exhibited unusual catalytic properties without stirring. Therefore, it was thought that the rate of this phase-boundary catalysis depends on the apparent area of the W/O interphase. To prove this, the reaction was carried out using reaction tubes with different bore sizes. Figure 3
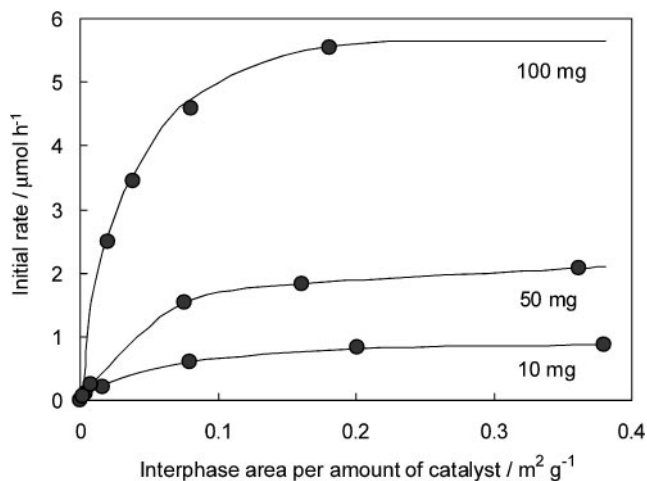
shows dependence of the initial rate of 1,2-epoxyoctane formation on apparent interphase area per unit weight of the catalyst (S/W in $m^2 \ g^{-1}$). Saturation of the initial rate was achieved at around 0.2 of S/W for all of the reactions with catalysts of different weights. These results clearly indicate that the reaction rate of the PBC system is determined by the area of the interphase where the catalyst particles lie. Therefore, the efficient and/or optimum amount of catalyst in this system can be controlled by the S/W ratio.

The above-mentioned results seem to be consistent with the mechanism of PBC based on the concept that amphiphilic catalyst particles, containing both hydrophilic and hydrophobic regions, are placed at the phase boundary to realize a continuous supply of H_2O_2 and organic substrates to the active sites on the particles without stirring. In the following sections, the advantageous features of the amphiphilic particles in various reaction conditions and/or systems are discussed.

Previous studies on selective oxidation reactions in conventional systems have shown that the use of a suitable cosolvent increases the concentration of olefin in aqueous H_2O_2 and improves mass transfer between aqueous and organic phases (4). Based on this idea, we prepared a homogeneous mixture containing 1-octene (8%), aqueous H_2O_2 (8%), and ethanol (84%) as a cosolvent to examine the catalytic activity of modified NaY catalysts under stirring and static conditions. Figure 4 shows the results. Under these conditions, no phase boundary was found, and all the catalysts were precipitated. As expected, for all catalysts, there were negligible effects of stirring on the yield of 1,2-epoxyoctane. Another point worth noting is that w/o-Ti–NaY showed the highest activity among these catalysts, as seen in the PBC conditions. This suggests that the amphiphilic nature of w/o-Ti–NaY, having higher affinity for both H_2O_2 and 1-octene, would improve the rate of reaction between them.

FIG. 3. Dependence of the amount of w/o-Ti-NaY catalyst particle occupied at an interphase on the initial rate of formation of 1,2-epoxyoctane.
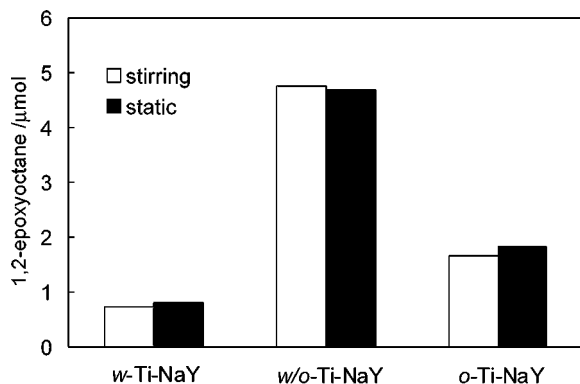

FIG. 4. The yield of 1,2-epoxyoctane in the presence of cosolvent. All reactions were carried out at room temperature for 20 h: 50 mg catalyst; 4 cm^3 of the mixture of 1-octene (8%), ethanol (84%), and 30% aqueous H_2O_2 (8%).
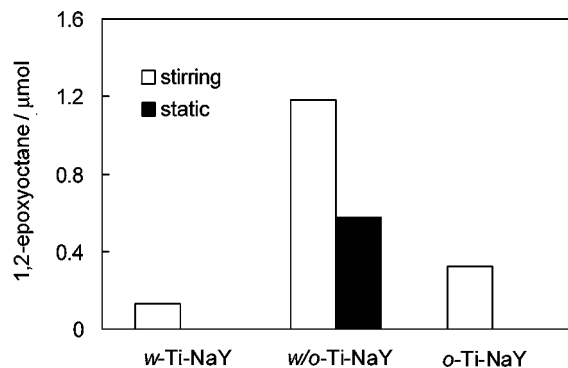
FIG. 5. Effect of stirring in the reaction in W/O mixture by using CCl_4 (6% 1-octene) and aqueous H_2O_2 mixture. All reactions were carried out at room temperature for 20 h: 50 mg of catalyst; 4 cm^3 of 1-octene/CCl_4 mixture; 1 cm^3 of aqueous H_2O_2 (30%) .

An amphiphilic catalyst could be used in a reversed W/O mixture. Figure 5 shows the yield of 1,2-epoxyoctane by modified NaY catalysts suspended in an aqueous H_2O_2/CCl_4 (6% of 1-octene) mixture. Due to the relatively high specific gravity, the organic CCl_4 phase by below the aqueous phase (i.e., the placement of organic–aqueous phases was inverted when compared with the 1-octene/H_2O mixture). Under these conditions, hydrophilic w-Ti–NaY was dispersed in the upper part, the aqueous H_2O_2 phase, as expected. On the other hand, the behaviors of o-Ti–NaY and w/o-Ti–NaY were completely different from those in the previous 1-octene/H_2O system; o-Ti–NaY immediately settled on the bottom part, the CCl_4 phase, and w/o-Ti–NaY was dispersed in the CCl_4 phase. These differences in distribution are attributed to the balance of hydrophobicity and density between the catalyst particles and the organic solvent. Detailed description of the characterization of these samples will be published elsewhere (12). The trend in activities of w/o-Ti–NaY, o-Ti–NaY, and w-Ti–NaY in the reversed system was similar to that observed in the 1-octene/aqueous H_2O_2 system, indicating that at the mesomeric level, the amphipilic region on w/o-Ti–NaY particles could enhance the adsorption of the oxidant and the substrate to react at the active Ti sites.

Extension of Substrates

Table 2 summarizes the results of catalytic epoxidation by w/o-Ti–NaY at ambient temperature with various straight-chain alkenes under stirring or static conditions. For all the alkenes used as substrates, corresponding epoxides were obtained as main products. Under static conditions, the yields of 1,2-epoxypentane and 1,2-epoxyheptane were ca. three times higher than those of 1,2-epoxyoctane and 1,2-epoxydodecane. The relatively high hydrophilicity and high reactivity of small alkenes could account for the different yields. On the other hand, under the condition of vigorous stirring, 1-pentene and 1-hexene gave even lower yields

of epoxides. Semiquantitative analyses revealed that by-products such as ketones (2-pentenal, 2-hexanal, 1-hexen-3-one, 2-pentanal, and 1-penten-3-one) and alcohols (corresponding to the reduced forms of the above ketones) are produced from these small alkenes, especially under the condition of vigorous stirring. Although no quantitative analysis has yet been performed due to the lack of authentic samples of these by-products, it is assumed that the total yield of epoxides is reduced by the mechanism of successive or parallel oxidation of alkenes under the condition of stirring. The PBC conditions seem preferable, to avoid an unexpected side reaction, since it allows the epoxidation to proceed without stirring.

Effect of Support and Model of the Reaction

The effect of support material on the PBC reactions was examined. Nonporous silica having a particle size almost the same as that of NaY zeolite (ca. 500 nm) was modified by a procedure similar to that used for the w/o-Ti–NaY preparation and used in reactions for epoxidation of 1-hexene, 1-octene, and 1-dodecene. As Fig. 6 shows, the modified NaY zeolite gave a higher yield of epoxides than did the silica-based catalysts, suggesting that the pores of the NaY particles are important.

As described above, w/o-Ti–NaY, having affinity for both hydrophobic and hydrophilic compounds, effectively catalyzed alkene epoxidation by using H_2O_2 as an oxidant even though the reaction was carried out under static conditions (i.e., without stirring or addition of a cosolvent). In the epoxidation of relatively reactive substrates, such as 1-pentene and 1-hexene, much higher yields of epoxide were obtained under static conditions. It was found that NaY, having a microporous structure with a relatively large surface area, was

TABLE 2

Epoxidation of Various Alkenes Using w/o-Ti–NaY^a

Entry	Substrate	Condition	Epoxide yield/μmol	By-products^b
1	1-Pentene	Static	51.3	Ketone,^{c} alcohol,^{d} diol^e
2	1-Pentene	Stirring	17.0	Ketone,^{c} alcohol,^{d} diol^e
3	1-Hexene	Static	51.6	Ketones,^{f} alcohols,^{g} diol^e
4	1-Hexene	Stirring	16.3	Ketones,^{f} alcohols,^{g} diol^e
5	1-Octene	Static	27.0	None
6	1-Octene	Stirring	27.4	None
7	1-Dodecene	Static	17.7	None
8	1-Dodecene	Stirring	20.0	None

^{a} Reaction conditions are the same as those given for Table 1.

^{b} Analyzed by gas chromatography–mass spectrometry.

^{c} 2-Pentenal.

^{d} 2-Penten-1-ol.

^{e} The amount of diol smaller than 1 μmol.

^{f} 1-Hexen-3-one, 4-methyl-1-pentene-3-one, 1-hexen-3-one, and 1-hepten-3-one.

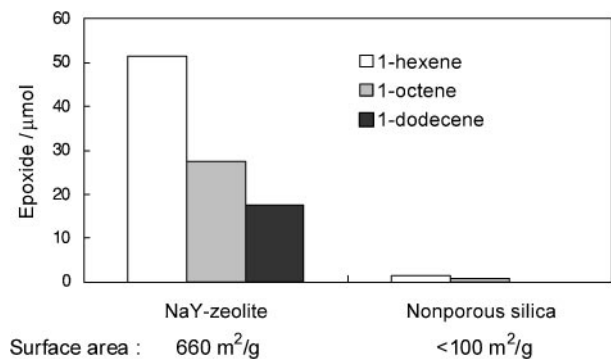^{g} 1-Hexene-3-ol and 1-octen-3-ol.

FIG. 6. Effects of catalyst support and substrate on the yield of the epoxides (1,2-epoxyhexane, 1,2-epoxyoctane, and 1,2-epoxydodecane) in the phase-boundary catalytic system.

preferable as a support in this system compared with non-porous silica with a smaller surface area. Furthermore, it should be noted that distribution of alkylsilyl groups on the external surface of w/o-Ti–NaY has been clarified by using fluorescence microscopy; each w/o-Ti–NaY particle has both hydrophobic and hydrophilic surfaces; i.e., one side is covered with alkylsilyl groups and the other is kept covered with hydroxyl groups (silanols). Details for this fluorescence microscopic study will be published elsewhere (12). On the basis of these results, a model of the PBC system is proposed (see Fig. 7). Although there is no experimental evidence for distribution of the Ti species at present, they should be attached to the external surface of NaY, since the estimated molecular size of Ti(OPr^i)$_4$ (ca. 1.5 nm), the source of Ti sites, is larger than the size of pore-entrance of NaY (ca. 0.17 nm). Thus, the modified particles are spontaneously located at the interphase in a W/O mixture with the hydrophobic side facing the organic phase and the hydrophilic side facing the aqueous phase.
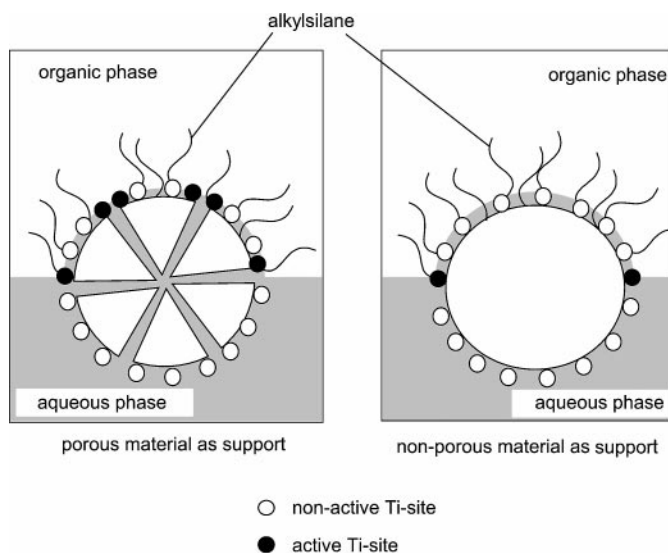

FIG. 7. Proposed model of an effective phase-boundary catalyst.

Consequently, active Ti sites on the NaY surface can be in contact with both organic substrates and aqueous H$_2$O$_2$. During the reaction at the Ti sites, due to the decrease in the concentration of substrates and H$_2$O$_2$ at the interphase, the concentration gradient of these reagents may appear in both organic and aqueous phases; this gradient may generate a driving force to supply these reagents from respective bulk solutions, thereby enabling the reaction to proceed efficiently without any enforced manipulation, such as stirring, in order to drive liquid–liquid mass transfer. In order to achieve this, the catalyst must satisfy the following requirements: (i) existence of active Ti sites at the liquid–liquid phase boundary, and (ii) continuous supply of both substrates and H$_2$O$_2$ through the hydrophobic and hydrophilic parts of the catalyst particles. Therefore, if the catalyst particles consist of nonporous materials, the number of Ti active sites are limited and efficient PBC cannot be expected. The use of a microporous material as a support must increase the effective interphase area of the catalyst (i.e., increase the number of active sites), resulting in higher activity.

It is noted that the apparent rate of epoxidation in the present system was much smaller than those previously reported (10, 11). The most likely reason for the lower activity is the presence of a smaller number of 4-coordinated Ti species, which is considered to be the real active species in olefin epoxidation reactions (13). In the present study, however, we employed a feasible process of Ti loading and did not optimize the yield of 4-coordinated Ti species in the preparation process. The impregnation of the titanium species used in this study also might induce aggregation to form titanium oxide, which is considered to decompose H$_2$O$_2$. Actually, it was observed that the molar amount of consumed H$_2$O$_2$ was ca. 1 mmol on w/o-Ti–NaY, while the epoxide yields were less than 100 μmol (Table 2); i.e., in the present system we obtained less than 10% efficiency of H$_2$O$_2$ utilization. Therefore, further studies on improvement and optimization of the activity of a phase-boundary catalyst are now underway in our laboratory.

CONCLUSIONS

The epoxidation reaction of alkene by partially alkylsilylated titanium-loaded zeolite with H$_2$O$_2$ has been demonstrated. Alkylsilylation can modify both the physical and catalytic properties of titanium-loaded zeolite. Partial covering with alkyl groups on the external surface of the zeolite catalyst gave amphiphilicity to the particles, enabling the location just at the W/O interphase of aqueous H$_2$O$_2$ and organic compounds to catalyze the epoxidation reaction. This PBC system is advantageous because of its simplicity. We have described efficient epoxidation reactions using the PBC system in this paper, and we are planning to apply the PBC system to other catalytic reactions, such as hydrolysis,

hydroxylation, and esterification, of water-immiscible organic compounds using water or reagents in their aqueous solutions.

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