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Citation	Journal of Catalysis, 204(2), 402-408 https://doi.org/10.1006/jcat.2001.3386
Issue Date	2001-12-10
Doc URL	https://hdl.handle.net/2115/14650
Type	journal article
File Information	JC2001-204-2.pdf



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

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Abstract

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 external surface of which was covered with hydrophobic alkyl groups and the rest was 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 lie at the liquid-liquid phase boundary between upper alkene and lower aqueous phases, and 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 co-solvent to make a homogeneous solution to drive the epoxidation. Yield of 1,2-epoxyoctane, a sole oxidation product from 1-octene, strongly depended on an apparent interphase area of the aqueous-organic phase-boundary. The amphiphilic catalyst exhibited much higher catalytic activity than those of hydrophilic titanium-loaded NaY, without modification by ODS, and hydrophobic one with almost full coverage by the alkyl groups. Similar trend of the activity among these catalysts was also observed when the reaction was carried out with vigorous stirring, in the presence of co-solvent, or in 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 applicable to epoxidation of other normal alkenes. Compared with nonporous silica particles, the use of microporous NaY with relatively high surface area gave a beneficial effect probably due to 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 was proposed.

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

Introduction

Nowadays, owing to increasing demand of clean and environmentally benign technologies in chemical process engineering, much attention has been paid for the establishment of ecologically more acceptable catalytic processes, including removal of toxic and expensive reagents, minimization of by-product formations, and simplification of workup procedure [1]. In liquid-phase epoxidation of olefins, e.g., various transition metal complexes are used practically as a homogeneous catalyst because they show high selectivity and activity. However, substitution of these homogeneous catalytic systems by heterogeneous ones is desirable because of their easiness of catalyst and product isolation from the reaction mixture and of possibility of operating the reaction continuously.

In order to realize cleaner oxidation process in liquid-phase, the selection of the oxidants is quite important. Hydrogen peroxide (H_2O_2) is one of the most promising oxidants because of its environmental implication; it gives only water as a product in a wide range of oxidation reactions. Moreover, it is less expensive and more accessible than the other oxidizing agents, such as organic peracids or hydroperoxides. Therefore, utilization of heterogeneous catalytic oxidation with aqueous H_2O_2 is 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. Addition of co-solvents, leading to a homogeneous solution, 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, presence of the third component, co-solvent, or the formation of the emulsion by stirring would make the workup procedures so much tedious.

Recently, we have proposed a new approach, named as phase-boundary catalysis (PBC), for catalyzing the liquid-liquid phase reaction by using solid catalyst and H_2O_2 under co-solvent-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

with neither adding the co-solvent nor making 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 the solid catalyst-H₂O₂ system similar to the PBC concept has been reported up to now. Here, we show the details of PBC for alkene epoxidation to clarify the mechanism and the catalytic properties.

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 received. Partly modified zeolite whose external surface was partly covered with alkylsilane was prepared in two steps. First, titanium(IV) tetra-2-propoxide (Ti(OPrⁱ)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/o*-Ti-NaY powder with water (50 wt%) was immersed in 10 cm³ 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 *w*-Ti-NaY surface, addition of small amount of water led to aggregation with 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 partly modified sample was labeled *w/o*-Ti-NaY. A similar procedure was also carried out for nonporous silica with 500 nm of the primary particle size (Nissan Chemical Industries), and it was labeled as *w/o*-Ti-silica.

Fully modified Ti-NaY (*o*-Ti-NaY) was prepared by a similar procedure as reported in ref. [7]. ODS (500 μmol) was dissolved in a mixed solution of toluene (80 vol%) and CCl₄ (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. The 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 literature [8] and modified with ODS. To the $\text{Ti}(\text{OPr}^i)_4$ (8 g)-ethanol (40 cm^3) solution, the 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 way same as that 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 the alkenes, purchased from Kanto Chemicals, were used as received. Because of the presence of appreciable amount of impurities, 1-octene was purified by passing through a column of basic alumina (Aldrich). 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 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 averse to dispersing in organic solvents, the *w*-Ti-NaY was dispersed well in the aqueous phase as expected (Fig. 1a). On the other hand, the *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 structure and hydrophilic feature of internal pore of these NaY particles were retained and the hydrophobic alkyl chains did not block the entrance of zeolite pores. These results agree well with the finding 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 stirring. All of the modified NaY catalysts showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane (entry 2-4), and the reaction did not occur without catalysts (entry 1). GC 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, partly modified catalyst (*w/o*-Ti-NaY, entry 3) showed much higher activity than 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 catalyst (entry 5).

Turnover number (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 ($10 \text{ } \mu\text{mol g}^{-1}$) (entry 9) gave 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 the higher catalytic activity in the aqueous-organic (*W/O*) mixture, it was still unclear that the observed reaction proceeds on whether Ti species loaded on NaY particles or those leached in reaction mixture. In order to exclude the latter possibility, the recovered and dried *w/o*-Ti-NaY catalyst after the 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% H₂O₂. The recovered *w/o*-Ti-NaY exhibits ca. 60% activity compared with the fresh *w/o*-Ti-NaY (entry 7) but 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. Decrease in activity, similar to the recovered *w/o*-Ti-NaY, could be observed when amorphous TiO₂ modified with ODS (*w/o*-Ti) in a similar procedure for the *w/o*-Ti-NaY preparation; the recovered and dried *w/o*-Ti showed decrease in the activities to ca. 75% (entry 9, 10). Therefore, the activity decrease 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 *w*-Ti-NaY showed appreciable activity only under the vigorous stirring, i.e., in the *W/O* emulsion, but was negligibly active without stirring. Similar behavior was seen in the *o*-Ti-NaY system in which the epoxide yield under static conditions was almost half of that of the stirred reaction mixture. On the other hand, the activity of *w/o*-Ti-NaY was independent on the stirring rate, i.e., this catalyst does not require the formation of *W/O* emulsion by stirring. The observation is one of the most striking characteristics of *w/o*-Ti-NaY and was completely different from the previously reported results for the co-solvent free "triphasic system" [9-11].

Thus, when *w/o*-Ti-NaY was added to the *W/O* mixture, it spontaneously lies at the phase boundary (see Fig. 1) and exhibited unusual catalytic properties without stirring. Therefore, the rate of this phase-boundary catalysis is expected to depend on apparent area of the *W/O* interphase. To prove this, the reaction was carried out using reaction tubes with different bore size. Figure 4 shows dependence of the initial rate of 1,2-epoxyoctane formation on apparent interphase area per unit weight of the catalyst (*S/W* in m² g⁻¹). The saturation of the initial rate was achieved at around 0.2 of *S/W* for all the case of reaction with different weight of the catalyst. These results clearly indicate that reaction rate of the PBC system is determined by the area of 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 well consistent with the mechanism of PBC based on the concept that the amphiphilic catalyst particles, containing both hydrophilic and hydrophobic regions, are placed at the phase boundary to realize continuous supply of H₂O₂ 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 is discussed.

Previous studies on selective oxidation reactions in the conventional systems have shown that the use of a suitable co-solvent increases the concentration of the olefin in aqueous H₂O₂ and improves mass transfer between aqueous and organic phases [4]. Based on this idea, we prepared a homogeneous mixture containing 1-octene (8%), aqueous H₂O₂ (8%), and ethanol (84%) as co-solvent to examine the catalytic activity of modified NaY catalysts under stirring and static conditions. Figure 3 shows the results. Under these conditions, no phase-boundary was found, and all the catalysts were settled down. As expected, for each catalyst, there were negligible effect of stirring on the yield of 1,2-epoxyoctane. Another point worth noting is that the *w/o*-Ti-NaY shows the highest activity among these catalysts, as seen in the PBC conditions. This suggests that the amphiphilic nature of the *w/o*-Ti-NaY having higher affinity for both H₂O₂ and 1-octene would improve the rate of reaction between them.

The amphiphilic catalyst could be used in reversed *W/O* mixture. Figure 5 shows the yield of 1,2-epoxyoctane by the modified NaY catalysts suspended in aqueous H₂O₂/CCl₄ (6% of 1-octene) mixture. Due to the relatively high specific gravity, organic CCl₄ phase lies below the aqueous phase, i.e., the placement of organic/aqueous phases was inverted when compared with the 1-octene/H₂O mixture. Under these conditions, the hydrophilic *w*-Ti-NaY was dispersed in the upper part, aqueous H₂O₂ phase, as expected. On the other hand, behavior of *o*-Ti-NaY and *w/o*-Ti-NaY was completely different from the previous 1-octene/H₂O system; *o*-Ti-NaY was immediately settled down on the bottom part, the CCl₄ phase, and *w/o*-Ti-NaY was dispersed in the CCl₄ phase. These differences in distribution

are attributable to the balance of hydrophobicity and density between the catalyst particles and the organic solvent. The detailed characterization of these samples will be published elsewhere [12]. Trend of activity 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 H₂O₂ system, indicating that, in mesomeric level, the amphiphilic region on the *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 substrate, corresponding epoxides were obtained as a main product. Under the static conditions, the yield of 1,2-epoxypentane and 1,2-epoxyheptane was 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 vigorous stirring, 1-pentene and 1-hexene gave even lower yield of epoxides. Semi-quantitative 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 form of above ketones) are produced from these small alkenes especially under vigorous stirring. Although at present no quantitative analysis was performed due to the lack of authentic samples of these by-products, we can assume the mechanism of successive or parallel oxidation mechanism of alkenes under stirring to reduce the total yield of epoxides. The PBC conditions seems preferable to avoid the unexpected side reaction, since it allows to drive the epoxidation without stirring.

Effect of support and model of the reaction

The effect of support material on the PBC reactions was examined. Nonporous silica having particle size almost same as that of NaY zeolite (ca. 500 nm) was modified by a procedure similar to that 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 the

yield of epoxides higher than the silica-based catalysts, suggesting the importance of the pores of the NaY particles.

As described above, the *w/o*-Ti-NaY, having affinity for both hydrophobic and hydrophilic compounds, effectively catalyzes alkene epoxidation by using H₂O₂ as oxidant even though the reaction was carried out under static conditions, i.e., without stirring or addition of co-solvent. Especially, in the epoxidation of relatively reactive substrates such as 1-pentene and 1-hexene, much higher yields of epoxide were obtained under static conditions. Moreover, it was found that the microporous structure of NaY having relatively higher surface area was preferable as a support in this system compared with the nonporous silica of lower surface area. On the basis of these results, a following model of the PBC system is presumed (Fig. 7). Since the estimated molecular size of Ti(OPrⁱ)₄ (ca. 1.5 nm), the source of active Ti sites, is larger than the size of pore-entrance of NaY zeolite (0.7 nm), the Ti species should be attached on the external surface. The alkylsilyl groups (though there is no experimental evidence and details will be published elsewhere [12]) is attached on a one-side of the external surface of NaY particle, leading to amphiphilicity of the particles. Thus, the modified particle are spontaneously located at the interphase in *W/O* mixture with facing the hydrophobic side to organic phase and the hydrophilic site to aqueous phase. Consequently, active Ti sites on NaY surface can be in contact with both organic substrates and aqueous H₂O₂. During the reaction at the Ti sites, due to the decrease in the concentration of substrates and H₂O₂ at the interphase, concentration gradient of these reagent may appear in both organic and aqueous phases; this gradient may generate a driving force to supply these reagents from respective bulk solutions, and thereby the reaction can 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: (1) existence of active Ti sites at the liquid-liquid phase-boundary, and (2) continuous supply of both substrates and H₂O₂ through the hydrophobic and hydrophilic parts of the catalyst particles. Therefore, if the catalyst particles consist of non-porous materials, the number of Ti active sites are limited and efficient PBC can not be expected. The use of microporous material as a support must increase the effective interphase area of catalyst, i.e., increase in

the number of active sites, resulting in the higher activity.

It is noted that the apparent rate of epoxidation in the present system was much smaller than those previously reported [10, 11]. One of the most probable reasons for the lower activity is the presence of less number of 4-coordinated Ti species which is considered to be the real active species in the olefin epoxidation reactions [13]. In the present study, however, we employed a feasible process of the Ti loading and have not optimized the yield of 4-coordinated Ti species in the preparation process. Further studies for the improvement and optimization of the catalytic activity of the phase-boundary catalyst are now being underway in our laboratory.

Conclusions

The epoxidation reaction of alkene by partly alkylsilylation titanium-loaded zeolite with H_2O_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_2O_2 and organic compounds to catalyze the epoxidation reaction. This PBC system is advantageous because of at least its simplicity. In this paper, we have shown the efficient epoxidation reactions, but the PBC system will be applied to the other catalytic reactions such as hydrolysis, hydroxylation or esterification etc., of water-immiscible organic compounds using water or reagents in their aqueous solutions.

Acknowledgments

H. N. thanks the Japan Society for the Promotion of Science (JSPS) for granting a Postdoctoral Fellowship. The authors are grateful to the Catalysis Society of Japan for the supply of zeolite samples. This research was partly supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 99302) from Ministry of Education, Science, Sports and Culture, Japan. Prof. Teruhisa Ohno (Osaka University) and Dr. Hisashi Semba (Nippon Shokubai Co. Ltd.) are acknowledged for their suggestions and stimulating discussion. The authors thank the Technical Division of Catalysis Research Center, Hokkaido University for

making the apparatuses.