



On Effective Locations of Catalytic Active Sites in Phase Boundary Catalysts

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Abstract. Zeolite loaded with alkylsilane-covered titanium oxide was found to be more effective than its nonporous silica counterpart as phase-boundary catalyst (PBC) to promote epoxidation of alkenes with aqueous hydrogen peroxide. It was demonstrated that the phase-boundary catalyst system required neither stirring to make an emulsion, nor addition of a cosolvent to make a homogeneous solution to drive the reaction. However, some basic facts about them remain unclear, such as the question as to where an effective location of the active sites of PBC resides: is it on the external surface of the catalysts, or in their pores? In order to elucidate this problem, TS-1, HZSM-5 and zeolite loaded with alkylsilane-covered sulfonic acid in which the location of the active sites is mainly inside the pore system, were chosen as model catalysts. Catalytic activities of the catalysts TS-1 and HZSM-5 were examined after modification with n-octadecyltrichlorosilane (ODS). Their activities were compared with zeolite loaded with alkylsilane-covered titanium oxide particles, in which the active sites are on the external surface in reactions of 1-octene with aqueous H₂O₂ and cyclohexene with water as model reactions. The study suggests that the location of the active sites on the external surface plays an important role in the phenomenon of phase-boundary catalysis.

Keywords: *location of catalytic active sites; phase-boundary catalysis.*

1 Introduction

Catalysts play an essential role in the refinery and chemical processing industries and for environmental control. Both economic and environmental issues are driving the new catalyst development and process improvements in catalysis [1,2]. Along this line, recently the novel concept of “phase-boundary catalysis” (PBC) has been proposed in order to utilize the immiscible liquid-liquid reaction system with solid catalysts [3-5]. This catalytic system offers advantages in terms of ease of separation, the possibility of continuous supply of immiscible substrates and working effectively without co-solvent.

In the PBC system the bimodal particles, containing both hydrophilic and hydrophobic regions, are placed at phase-boundary in order to catalyze the reaction without requiring a catalyst emulsion or stirring. This phenomenon was observed when zeolites loaded with alkylsilane-covered titanium oxide were used in the epoxidation of alkenes with aqueous H_2O_2 [3-5]. It has been found that only partial coverage of hydrophobic alkylsilyl was needed to achieve high catalytic activity. Catalytic activity was low when non-porous silica was used instead of zeolite as catalyst support, suggesting that the pores might play a role in the catalytic reaction [4]. It was clarified that the characteristic behavior of phase-boundary catalysts can be attributed to an appropriate balance of hydrophilicity and hydrophobicity [5]. The current strategy is different from those previously reported for trimethylsilylated titanosilicate [6,7], because the previous strategy was merely to create a hydrophobic environment on titanium active sites to inhibit the adsorption of excessive water.

Previously, we have developed a PBC by using titanium isopropoxide $\text{Ti}(\text{OPr}^i)_4$ impregnated in the external surface of NaY zeolite [3-5]. As this PBC has been known to catalyze the epoxidation of alkenes by aqueous H_2O_2 [3-5], we were interested in further exploring the effective location of the active sites. Here, we report our attempts to find evidence for effective active sites and obtain general criteria for the optimisation of the catalysts with respect to the location of the active sites in PBC. In this experiment, two kinds of catalysts were used, and modified with *n*-octadecyltrichlorosilane (ODS). TS-1, HZSM-5 and sulfonic acid functionalized zeolite have been chosen as model catalysts in which the active sites are mainly located inside the pore system. Their catalytic performance was compared with that of titanium-oxide zeolite with the active sites mainly located on the external surface. As model reactions we used the epoxidation reaction of 1-octene with aqueous hydrogen peroxide and cyclohexene with water.

2 Experiments

2.1 Catalyst Preparation

2.1.1 Alkylsilylated Ti-NaY, TS-1 and HZSM-5

NaY zeolite (JRC-Z-Y5.5) and HZSM-5 (JRC-Z5-90H(1)) powders were supplied by the Catalysis Society of Japan and used as received. TS-1 was a gift from Prof. T. Tatsumi of the Tokyo Institute of Technology, Japan. NaY zeolite covered titanium oxide (Ti-NaY) was prepared by impregnation of $\text{Ti}(\text{OPr}^i)_4$ according to the literature [3-5]. The molar amount of Ti was $500 \mu\text{mol g}^{-1}$ zeolite. Modified Ti-NaY, TS-1 and HZSM-5, with their external surfaces partially covered with alkylsilane, were prepared [3-5]. Unmodified Ti-NaY, TS-1 and HZSM-5 are denoted as w-Ti-NaY, w-TS-1 and w-HZSM-5

respectively. Modification of Ti-NaY with alkylsilane was typically performed as follows: the w-Ti-NaY powder containing water (0.5 g per 1.0 g of w-Ti-NaY) was immersed in 5 ml toluene containing 500 μmol of *n*-octadecyltrichlorosilane (ODS, ShinEtsu), and this suspension was shaken for ca. 5 min at room temperature. The solid was collected after centrifugation and dried at 383 K for 5 hours. The partially modified sample is labeled w/o-Ti-NaY. A similar procedure was carried out for TS-1 and HZSM-5, which are labeled w/o-TS-1 and w/o-HZM-5 respectively.

Fully modified Ti-NaY (o-Ti-NaY) was prepared without the addition of water. A similar procedure was carried out for TS-1 and HZSM-5, which are labeled o-TS-1 and o-HZSM-5, respectively.

2.1.2 Alkylsilylated Propylsulfonic Acid NaY

Sulfonic acid covered NaY zeolite was prepared according to the literature [8]. In a typical experiment, NaY zeolite was initially calcined at 400 °C for 2 h prior to modification in order to remove adsorbed water. Calcined NaY zeolite (3 g) was added to a solution of 3-mercaptopropyl trimethoxysilane (MPTS, Wako) (0.294 g) dissolved in toluene (20 ml) as the organosulfonic acid precursor. The molar amount of sulfonic acid (SO_3H) was 500 $\mu\text{mol g}^{-1}$ zeolite. Toluene was dried over zeolite 4A prior to use. After 4 h reflux, the powder was collected and washed with $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (1:1) (50 ml) and air-dried.

Materials with immobilized mercaptopropyl groups were typically oxidized with H_2O_2 in a methanol-water mixture, 6 ml of 30% H_2O_2 dissolved in 18 ml methanol. After 24 h, the suspension was filtered, and washed with H_2O and EtOH. The wet materials were resuspended (3 wt%) in 0.1 M H_2SO_4 for 2 h. Finally, the materials were extensively rinsed with H_2O and dried at 333 K under vacuum. These acid materials are denoted as $\text{SO}_3\text{H-NaY}$.

Partly modified $\text{SO}_3\text{H-NaY}$, with the external surface partly covered by alkylsilane from ODS, was prepared with the same procedure to give w/o-TS-1, and is labeled w/o- $\text{SO}_3\text{H-NaY}$. Unmodified and fully modified $\text{SO}_3\text{H-NaY}$ are labeled w- $\text{SO}_3\text{H-NaY}$ and o- $\text{SO}_3\text{H-NaY}$, respectively.

2.1.3 Passivation of the External Surface of HZSM-5

Passivation of the external surface of HZSM-5 was processed in two steps. During the first step, *n*-octadecyltrichlorosilane (ODS) was attached with full coverage, using a procedure similar to the one for making o-Ti-NaY. In the second step, the powders obtained were calcined at 500°C for 5 hours in order to coat the external surface of HZSM-5 with a silica layer. The obtained solids were further modified with ODS using a similar procedure to the one used for

the preparation of w/o-Ti-NaY and o-Ti-NaY. They are labeled w-Si-HZSM-5, w/o-Si-HZSM-5 and o-Si-HZSM-5, respectively.

2.2 Dispersion Behavior and Determination of Adsorbed Water

The dispersion behavior of modified NaY particles was carried out in a UV-vis cuvet containing 1-octene. Typically, 10 mg of a solid sample was added to 1-octene (4 ml) and shaken vigorously prior to UV-vis measurements. The transmittance at 400 nm was used as a reference. The transmittance during precipitation was taken as a function of time by a UV-Vis Hewlett Packard 8453.

The adsorption of water was carried out as follows: about 1 g of NaY sample was dehydrated under vacuum at 100 °C overnight. After dehydration, the sample was exposed to water vapor at room temperature, followed by the determination of the percentage of adsorbed water.

2.3 Reaction Conditions

Epoxidation of 1-octene was carried out using the prepared catalysts. Typically, 1-octene (2 ml), 30% aqueous H₂O₂ (0.5 ml, Wako pure chemicals), and catalyst powder (25 mg) were placed in a glass tube, and the reaction was performed with or without stirring for 20 h at room temperature. The molar ratio of 1-octene to Ti active species was 0.000984. Hydroxylation of cyclohexene was carried out as follows: cyclohexene (2 ml), water (2 ml) and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with or without stirring at 70 °C for 20 h after removal of oxygen by Argon bubbling. Hydration of 1,2-epoxyoctane (1 ml) with water (1 ml) using a catalyst powder (25 mg) was also carried out at 70 °C for 20 h with and without stirring. The products of the above reactions were analyzed by gas chromatography (Shimadzu GC-14B with FID and DB-1 column).

3 Results and Discussion

3.1 Dispersion Behavior

The dispersion behavior of w-Ti-NaY, w/o-Ti-NaY and o-Ti-NaY was examined by UV-vis. Figure 1 shows the precipitation rate of these catalysts. The o-Ti-NaY was still well-dispersed in 1-octene after 35 minutes, whereas w/o-Ti-NaY quickly precipitated in the first 5 minutes. In contrast, the w-Ti-NaY was averse to dispersion in 1-octene due to its hydrophilicity. When these catalysts were dispersed in the mixture of 1-octene and water, compared to o-Ti-NaY, almost all of the w/o-Ti-NaY particles were located at the phase boundary, while the w-Ti-NaY was dispersed in aqueous phase. However, the

distribution of alkylsilylated particles could not be examined by this method, to determine whether w/o-Ti-NaY contains some o-Ti-NaY or vice-versa.

When the above immiscible mixture was used for w-TS-1, w/o-TS-1, o-TS-1 (alkylsilylated TS-1), and for w-HZSM-5, w/o-HZSM-5, o-HZSM-5 (alkylsilylated HZSM-5), the same dispersion behavior as with w-Ti-NaY, w/o-Ti-NaY and o-Ti-NaY was observed. This behavior was also exhibited in the mixture of cyclohexene-water.

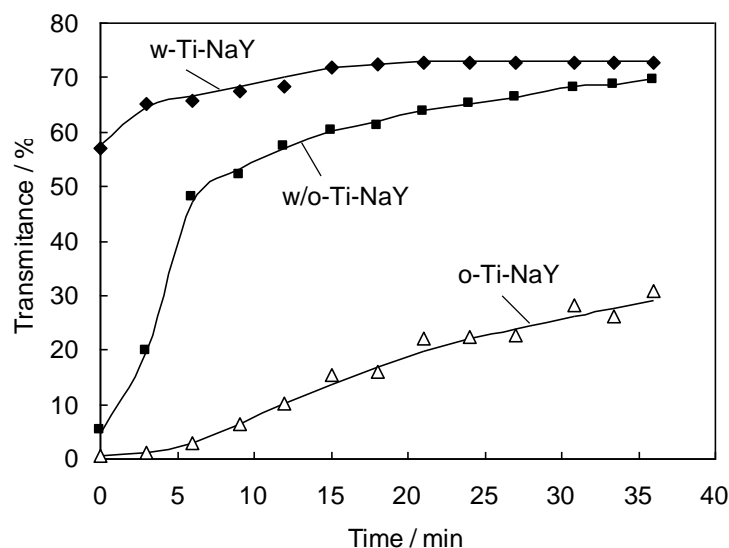


Figure 1 Percentage of transmittance at 400 nm during precipitation of w-Ti-NaY, w/o-Ti-NaY and o-Ti-NaY dispersed in 1-octene.

3.2 Active Sites on the External Surface of Zeolite

In previous studies [3-5], the PBC phenomenon was clearly demonstrated by w/o-Ti-NaY. To complete this study, the role of hydrophilic internal pores and partial hydrophobic coverage of the external surface of zeolites is described below.

The reactivity of modified zeolite was investigated by gradual addition of aqueous H_2O_2 in a regular interval of time (Figure 2). In these catalytic systems, partial modification by alkylsilane (w/o-Ti-NaY) gave better activity than full modification (o-Ti-NaY). When w-Ti-NaY was used as catalyst, the reaction was saturated after about 1 hour. In the case of o-Ti-NaY, an increase of the formation of 1,2-epoxyoctane at the same rate after the second and third addition of aqueous H_2O_2 suggests that the H_2O_2 consumption by the catalyst is the reason for the saturation. It is also considered that there was no catalysis in

the epoxidation reaction over w-Ti-NaY, because there was no increase in the formation of 1,2-epoxyoctane. This phenomenon can be explained by the occurrence of gradients of concentration in the mass transfer of aqueous H_2O_2 . The high concentration gradient of the transferred aqueous H_2O_2 is created by the hydrophilic and hydrophobic part of the w/o-Ti-NaY particles. This did not occur with o-Ti-NaY because there was no concentration gradient as its pores were totally filled with aqueous H_2O_2 , i.e. the activity did not increase after the fourth addition of aqueous H_2O_2 (see Figure 2). On the basis of the chemical phenomena occurring during gradual addition of aqueous H_2O_2 , it can be suggested that the hydrophilic pore system and the hydrophobic external surface of zeolite play a significant role in supplying the aqueous substrate and the organic substrate to the active site, which is located on the external surface of zeolite. However, the necessity of the location of the active sites on the external surface of zeolite remains unclear. The important role of the location of the active sites in PBC is described in the following sections.

3.3 Active Sites inside the Pores of Zeolite

In the above discussion, we used Ti species which were impregnated on the surface of NaY zeolite (Ti-NaY). There is no doubt that the Ti-species are mostly located at the external surface of the zeolite, because the molecular size of $\text{Ti}(\text{OPr})_4$ (ca. 1.5 nm) as Ti source is larger than the pore size of NaY zeolite (ca. 0.7 nm). In the TS-1 catalyst, the Ti-atoms are located dominantly inside the pores of the zeolite, and not on the external surface [9]. As can be seen in Figure 3, modification of TS-1 by alkylsilane led to a significant catalytic rate enhancement under static conditions. In this condition – since no difference of activity could be observed for the systems containing w/o-TS-1 and o-TS-1 – a significant difference was shown in the activity of unmodified and alkylsilated TS-1. This enhancement might be attributed to the location of the catalyst during the reaction. The o-Ti-NaY could also have settled down at liquid-liquid boundary after ca. 3 hours. However, under stirring conditions catalytic activity was not so different between the modified and the unmodified TS-1 catalysts. Because the addition of a small amount of water is necessary before the attachment of alkylsilyl groups for making a bimodal amphiphilic surface structure of zeolite, the catalytic activity of w/o-TS-1 prepared with different amounts of water was also examined. No effect was observed of this amount of water on the activity of these catalysts under static or stirring conditions.

As shown in Table 1, in the absence of mechanical agitation all modified TS-1 catalysts showed a lower activity compared to vigorous stirring. Although pore diffusion does not depend on the substrate's velocity outside the catalyst particles, the decrease of the epoxidation rate of alkene under static conditions is controlled by the concentration gradient of the reactants and the products induced by stirring [10]. The catalytic rate is increased by mechanical agitation.

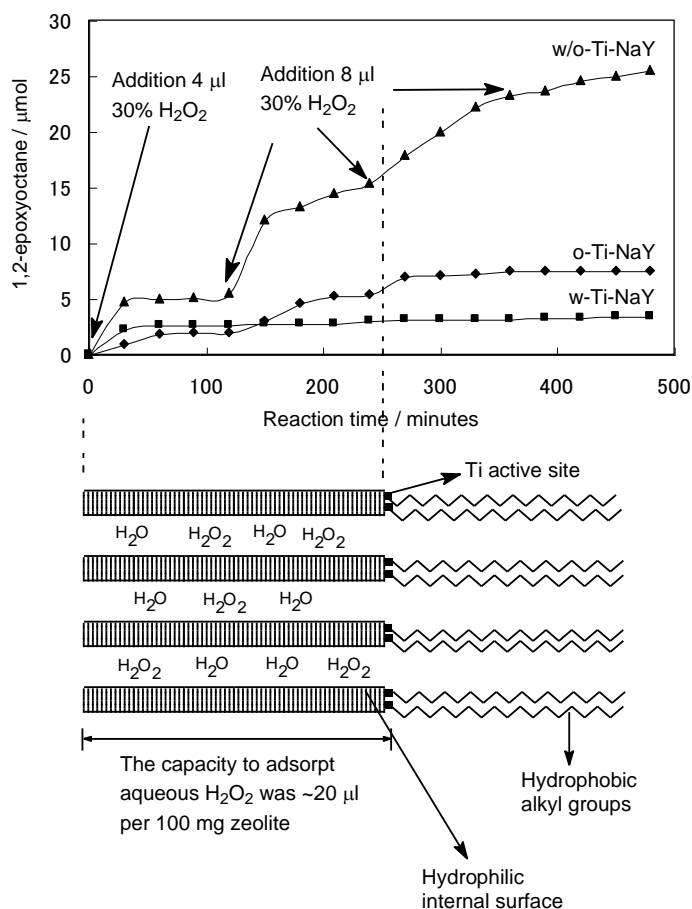


Figure 2 Effect of amount of H_2O_2 added to the amount 1,2-epoxyoctane produced over w/o-Ti-NaY, o-Ti-NaY and w-Ti-NaY. The reaction was carried out with 1-octene (8 ml) and catalyst (100 mg).

Although there are some indications that the most active Ti-species in w/o-Ti-NaY that contributed to the PBC phenomena were located on the external surface of the catalyst, its activity was lower compared to modified TS-1. The TS-1 may inherently be more active than Ti-NaY, as shown by the yield of 1,2-epoxyoctane. This effect may be accentuated by the nature of the active sites of the Ti species in TS-1. It is generally believed that the higher activity and selectivity for the formation of epoxide is due to the presence of isolated 4-coordinated Ti-species [9,11-14]. In this study, the impregnated Ti species in Ti-NaY can be considered to be present in the form of aggregates containing a smaller number of 4-coordinated and inactive inner Ti species.

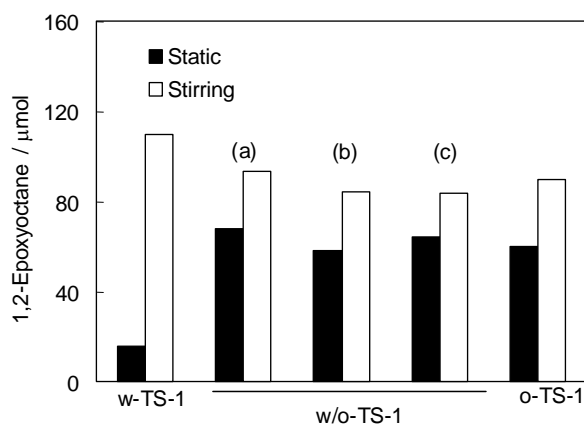


Figure 3 The yield of 1,2-epoxyoctane in the presence of modified TS-1 with and without vigorous stirring for 20 h at room temperature. The w/o-TS-1 was prepared with the addition of a different amount of water; (a) $500 \mu\text{l g}^{-1}$, (b) $750 \mu\text{l g}^{-1}$ and (c) $1000 \mu\text{l g}^{-1}$ zeolite before modification with ODS. Composition of the mixture: 25 mg catalyst, 0.5 ml 30% H_2O_2 and 2 ml 1-octene.

In order to obtain general criteria for the optimisation of the catalysts with respect to the location of the active sites, it is necessary to extend the catalytic models for other catalysts and active sites. For this purpose alkylsilylated HZSM-5 particles were used. As shown in Table 1, cyclohexanol was the major product in the conversion of cyclohexene with water over w-HZSM-5, w/o-HZSM-5 and o-HZSM-5. The results (see Table 1) show that HZSM-5 catalysts display a trend similar to the catalytic activities with TS-1 catalysts (Figure 3). These results suggest that the same location of active sites in TS-1 and HZSM-5 has the same effect on their catalytic activity. However, the role of the external active sites is still not clearly shown. Based on this consideration, the role of the external active sites in the reaction can be examined by passivation of the external surface of zeolite by coating it with a silica layer. This layer is considered not active toward the hydroxylation of cyclohexene. Table 2 shows the trend of the catalytic activity of w-Si-HZSM-5, w/o-Si-HZSM-5 and o-Si-HZSM-5 (passivated HZSM-5). Although the results in Table 2 show no significant effect of this approach on the trend of the activities of these catalysts, the activities of these catalysts were ca. 5% lower compared to the unpassivated HZSM-5 catalysts (Table 1). This suggests that the active sites located on the external surface contributed to increasing the activity. However, the contribution of the external acid sites to the overall reaction was small.

Catalytic activities in Figure 3 and Table 1 show that stirring was still necessary to enhance the activity of w/o-TS-1 and w/o-HZSM-5. This might be affected

by the intrinsic properties of TS-1 and HZSM-5, i.e. the existence of active sites incorporated in their framework and the MFI structure of their framework.

Table 1 The yield of cyclohexanol in organic phase on the hydroxylation of cyclohexene using various modified HZSM-5 under static and stirring conditions.^a

Catalyst	Cyclohexanol yield / μmol	
	stirring	static
w-HZSM-5	56.1	28.0
w/o-HZSM-5	39.4	29.1
o-HZSM-5	38.9	28.1

^a All reactions were carried out at 70 °C in argon atmosphere for 20 h: 50 mg catalyst; 2 ml cyclohexene and 2 ml water.

These properties gave a synergistic effect for the catalytic activities with hydrocarbons [15]. In order to exclude the possibility of these characteristics, sulfonic acid (SO_3H) anchored on the surface of NaY zeolite was used as model catalyst. The source of SO_3H was 3-mercaptopropyl trimethoxysilane (MPTS). This catalyst was used for acid catalysis in a system containing cyclohexene and water. Since the molecular size of MPTS is smaller than the pore size of NaY zeolite according to the literature, it is expected that SO_3H is mainly anchored on the internal surface of NaY zeolite by a supercritical fluid silylation process [16]. Our silylation process was different because we performed it at room temperature and under atmospheric pressure. One might expect that the deposition of silanes on the external surface is also favorable.

Table 2 The yield of cyclohexanol in organic phase on the hydroxylation of cyclohexene using various modified HZSM-5 under static and stirring conditions.^a

Catalyst	Cyclohexanol yield / μmol	
	stirring	static
w-Si-HZSM-5	50.4	42.3
w/o-Si-HZSM-5	40.2	39.4
o-Si-HZSM-5	20.8	24.2

^a Reaction conditions: same as given for Table 1.

As shown in Table 3, all the systems containing modified sulfonic acid functionalized zeolite (w- SO_3H -NaY, w/o- SO_3H -NaY and o- SO_3H -NaY) produced 2-methyl-2-cyclopenten-1-one as a major product. A similar compound was also observed when 0.1 M H_2SO_4 was used instead of the

catalyst under the same experimental conditions (Table 3). With w/o-SO₃H-NaY, under stirring conditions, the activity (i.e. the peak area of the 2-methyl-2-cyclopenten-1-one per amount of SO₃H) more than tripled compared to the mixture containing H₂SO₄ (Table 3). This indicates that the w/o-SO₃H-NaY is particularly capable of catalyzing the reaction at the liquid-liquid phase-boundary. However, the mechanism of this reaction was not fully understood. It could be that carbenium ion and ring contraction mechanisms occurred [17]. In order to investigate heterogeneity, the catalysts were suspended in water and stirred for 2 h at 70 °C. After filtration, the water, without the catalyst, was vigorously stirred for 20 h with the addition of cyclohexene. This system exhibits no activity. This suggests that the reaction occurs on the catalyst particles, but not due to the leached SO₃H species. It should be noted that mass transfer limitations may place a constraint on SO₃H-NaY catalysis because the location of SO₃H as the active site is mainly inside the pores of NaY (Table 3). These mass transfers are further enhanced by mechanical agitation.

Table 3 The yield of 2-methyl, 2-cyclopenten-1-one in organic phase chromatogram on the reaction of cyclohexene with water using various modified SO₃-NaY, under static and stirring conditions. ^a

Catalyst	2-methyl, 2-cyclopenten-1-one / a.u.	
	stirring	static
w-SO ₃ H-NaY	35	20
w/o-SO ₃ H-NaY	65	41
o-SO ₃ H-NaY	40	30
0.1 M H ₂ SO ₄	170	0

^a Due to a lack of the authentic sample, the yield was calculated from the peak area of 2-methyl, 2-cyclopentene-1-one in chromatogram. Reaction was also carried out with acidified aqueous phase (0.1 M H₂SO₄). Reaction conditions: same as given for Table 1.

For comparison, modified SO₃H-NaY catalysts were also used to catalyze the conversion of 1,2-epoxyoctane to 1,2-octanediol; the results are shown in Table 4. It showed that the activity of modified SO₃H-NaY was also always higher when mechanical agitation was applied to the system. Similar to the conversion of cyclohexene (Table 3), the results in Table 4 show that w/o-SO₃H-NaY also gave a higher activity compared to w-SO₃H-NaY and o-SO₃H-NaY. One possible explanation is that the amount of SO₃H on the external surface is high, which gives a larger contribution to the activity of the catalyst.

Based on these results and the previously discussed results, it is suggested that alkylsilylation on the external surface of zeolite, in which the active sites are mainly located inside the pores, cannot change the mode of the catalytic action;

it is still necessary to stir the reaction mixture to drive the mass transfer of substrates and reagents. The external surface of zeolite is an effective location for active sites in the PBC system, in which the active sites (as well as the catalyst) are placed at the interface between organic substrate and aqueous phase by a partial alkylsilylation of catalyst particles to drive the reaction without stirring.

Table 4 The yield of 1,2-octanediol in organic and aqueous phases on the hydration of 1,2-epoxyoctane using various modified SO₃H-NaY under static and stirring conditions.^a

Catalyst	1,2-octanediol yield / μmol	
	stirring	static
w-SO ₃ H-NaY	122.3	0.1
w/o-SO ₃ H-NaY	140.4	83.5
o-SO ₃ H-NaY	24.2	0.1

^a All reactions were carried out at 70 °C for 20 h: 25 mg catalyst; 1 ml 1,2-epoxyoctane and 1 ml water. The yield was subtracted from the control experiment.

4 Conclusions

Our experiment investigating the possible location of active sites using model catalysts shows that the active sites on the external surface of microporous catalysts play an important role in phase-boundary catalytic action. Stirring is not rate limiting towards catalytic activity. However, catalytic efficiency is not directly correlated to the location of the active sites and is particularly dependent on the nature of the active sites.

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