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Phase-boundary catalysis: a new approach in alkene epoxidation with hydrogen peroxide by zeolite loaded with alkylsilane-covered titanium oxide

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An NaY zeolite, modified with partly alkylsilane-covered titanium oxide and located at the boundary between aqueous and organic phases (a phase-boundary catalyst), acts as a catalyst for alkene epoxidation without stirring or the addition of a co-solvent to drive liquid–liquid phase transfer.

Utilization of hydrogen peroxide (H_2O_2) as an oxidant for organic substrates has received much attention in recent years because of its environmental implications; 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. However, H_2O_2 is generally supplied as an aqueous solution, and when the substrate to be oxidized is insoluble in water, it is necessary to add a co-solvent to obtain a homogeneous reaction mixture.[1,2] Here, we propose a novel integrated chemical system, which we have termed ‘phase-boundary catalysis’, using aqueous H_2O_2 for the oxidation of organic compounds without any co-solvent. For this system, a particulate zeolite catalyst has been designed and prepared in order to be placed at the phase boundary between aqueous H_2O_2 and an organic substrate. Several authors have reported a ‘triphase system’ in which the homogeneous modification of a particulate catalyst loaded with metal ions or their complexes as active sites induced or accelerated the oxidation of organic substrates with H_2O_2 in aqueous solution.[3–7] In such triphase systems, however, vigorous stirring, leading to sufficient mass transfer, is required to drive the reaction. However, our strategy is different from those previously reported because we aim at placing the bifunctional particles, containing both hydrophilic and hydrophobic regions, at the phase boundary in order to catalyze the epoxidation reaction without requiring an emulsion containing the catalyst by stirring.

Modified zeolite on which the external surface was partly covered with alkylsilane was prepared in two steps. First, titanium(IV) tetraisopropoxide [$Ti(OPr^i)_4$, Wako Pure Chemical] was impregnated from benzene solution into NaY zeolite powder (JRC-Z-Y5.5, supplied by the Catalysis Society of Japan) and heated at 383 K overnight to give sample W-Ti-NaY. 500 μmol of Ti was used per gram of NaY unless otherwise stated. In the second step, *n*-octadecyltrichlorosilane (OTS, Tokyo Kasei) in toluene was impregnated into the W-Ti-NaY powder containing water (0.5 cm^3 g per g of NaY) and heated at 383 K overnight. Due to the hydrophilicity of the W-Ti-NaY surface, addition of a small amount of water (0.5 g per g of W-Ti-NaY) led to aggregation owing to the capillary force of water between particles. Under these conditions, it is expected that only the outer surface of aggregates, in contact with the organic phase can be modified with OTS, and indeed almost all of the particles were located at the phase boundary when added to an immiscible water–organic solvent (W/O) mixture. The partly modified sample is denoted W/O-Ti-NaY. Fully modified Ti-NaY (O-Ti-NaY), prepared without the addition of water in the above second step, is readily suspended in an organic solvent as expected. At present, it is not clear whether the position of alkylsilane attachment is on the zeolite, on the Ti oxide (hydroxide), or on both.

In the water adsorption experiment at room temperature, it was observed that the adsorption capacity of modified zeolites (8 mmol g^{-1} for both W/O-Ti-NaY and O-Ti-NaY) was not greatly different from that of the parent NaY zeolite (11 mmol g^{-1}), suggesting that alkylsilane modification did not block the pores of zeolites. This observation is in agreement with the finding reported by Singh and Dutta.[8]

Oct-1-ene (Kanto Chemical, 97%) was purified by passing it through a column of basic alumina and was used as a substrate for epoxidation reaction. Typically, oct-1-ene (4 ml), 30% aqueous H_2O_2 (1 ml) and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with or without stirring for 20 h at ambient temperature. As can be seen in Table 1, all of the modified zeolites showed activity for epoxidation of oct-1-ene to give 1,2-epoxyoctane. GC analyses (Shimadzu GC-14B) indicated that 1,2-epoxyoctane was the sole product, and other probable by-products, such as octanone, octan-1-ol, octan-2-ol or octane-1,2-diol, were not produced. NaY modified by Ti-species only (W-Ti-NaY) was hydrophilic in nature, and was suspended in water when added to a W/O mixture. W-Ti-NaY showed appreciable epoxidation ability only under vigorous stirring, *i.e.* in the W/O emulsion, but was negligibly active without stirring, as shown in Fig. 1. Modification of Ti-NaY by alkylsilane led to a significant rate enhancement. In particular, partial modification by alkylsilane (W/O-Ti-NaY, entry 3) led to better activity than full modification (O-Ti-NaY, entry 4). A reference experiment using non-porous silica (Wako Pure Chemical, < 200 mesh) was also carried out. Silica was modified in a similar manner to that of W/O-Ti-NaY. The epoxidation result showed that the yield of 1,2-epoxyoctane was lowered ten-fold compared to W/O-Ti-NaY (entry 8), suggesting that the pores might be playing a role in the catalytic reaction.

Table 1 Catalytic room-temperature epoxidation of oct-1-ene[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	(Solution)[b]	0.1	—
6	W/O-Ti-NaY (reused)[c]	16.4	0.7
7	W/O-Ti-NaY[d]	22.7	45.4
8	W/O-Ti-silica[e]	2.9	0.1

[a] All reactions were carried out at room temperature for 20 h with oct-1-ene (4 ml), 30% H_2O_2 (1 ml) and catalyst (50 mg) with vigorous stirring; the concentration of Ti and alkylsilane = 500 μmol g^{-1}. [b] The aqueous phase of entry 3 after the reaction. The reaction was conducted for 9 h. [c] The reaction was performed after washing and drying of the catalyst. [d] Concentration of Ti = 10 μmol g^{-1}. [e] Nonporous silica (Wako Pure Chemical, < 200 mesh) was modified in a similar way to that of W/O-Ti-NaY.

The recovered and dried W/O-Ti-NaY catalyst was reused in a fresh W/O mixture and showed *ca.* 60% activity. To the remaining reaction mixture, without the catalyst, was added 30% H_2O_2 aqueous solution, and the mixture was vigorously

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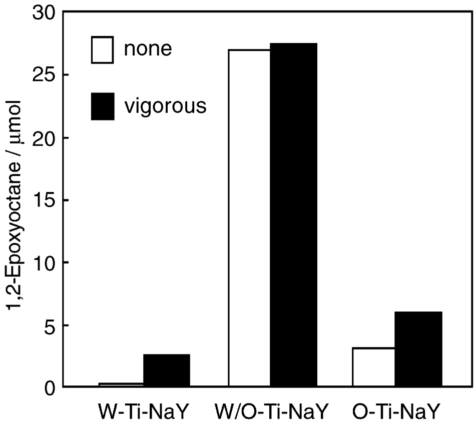

Fig. 1 Effect of stirring on the yield of 1,2-epoxyoctane.

stirred at ambient temperature. A negligible increase in the amount of epoxide could be seen. These facts suggest that epoxide formation occurs at the phase boundary, and not from any leached Ti species. Although the 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) for relatively larger Ti loading, W/O-Ti-NaY with a lower Ti concentration (10 µmol g^{-1}) (entry 7) gave a TON of *ca.* 45, indicating catalytic action of the Ti species. Higher loading might induce aggregation leading to inner inactive sites. One of the most striking features of W/O-Ti-NaY is shown in Fig. 1; the partial alkylsilane modification not only enhanced the epoxidation but also changed the mode of reaction. As described above, W-Ti-NaY showed activity only under vigorous stirring, and a similar behavior was seen for 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 not dependent on the stirring rate, *i.e.* this catalyst does not require the formation of W/O emulsion, completely at variance with previously reported results for the 'triphase system'.[7] The amphiphilic nature of W/O-Ti-NaY, enabling it to sit just at the W/O phase boundary, may account for the constant activity. Therefore, the rate of this phase-boundary catalysis depends only on the apparent area of the W/O interphase. In fact, when a narrow-bore reaction tube was used to decrease the apparent interphase area, the activity was reduced, as expected (data not shown).

All of the results mentioned above seem consistent with the mechanism of phase-boundary catalysis; amphiphilic particles having active sites (Ti-species) lie at the W/O interphase to catalyze the chemical reaction. However, the apparent rate of epoxidation was much lower than those previously reported.[4] One of the reasons for the low activity in our catalysts is the presence of few four-coordinate Ti species which are considered to be the most active species in olefin epoxidation.[9] It should be noted that we used the Ti-loaded NaY zeolite as an easily available material and the catalyst and the reaction conditions have not been optimized. Further study for improvement of catalytic activity by generating four-coordinated Ti species in the catalytic system is now underway. Thus, we have shown a new concept of phase-boundary catalysis, that is applicable when amphiphilic particles, molecular assemblies, or films with adequate active sites are used, to a wide range of catalytic reactions.

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