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Effect of Titanium Active Site Location on Activity of Phase Boundary Catalyst Particles for Alkene Epoxidation with Aqueous Hydrogen Peroxide

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Abstract

Epoxidation of 1-octene with hydrogen peroxide at room temperature was examined using bimodal zeolite particles, in which some of the external surfaces some were covered with hydrophobic alkyl groups and the rest were left hydrophilic. When bimodal titanium-loaded NaY were added to a mixture of aqueous hydrogen peroxide and 1-octene, these particles could be assembled just at the liquid-liquid phase boundary, resulting in the formation of a particulate film, and efficiently catalyzed the epoxidation of 1-octene even without agitation. On the other hand, when TS-1 particles in which the active titanium species located mainly inside the pore system were used, there were no significant effects of partial modification on catalytic activity under the conditions of both stirring and no stirring. These results suggested that titanium species located on the external surfaces of particles were dominantly effective for the observed phase boundary catalytic system.

1. INTRODUCTION

There has been an increasing demand for the development of environmentally benign and ecologically more-acceptable methods for production of organic fine chemicals. Substitution of chemical reaction systems with stoichiometric reagents by heterogeneous catalytic reaction systems is desirable because of the simplicity of isolation of a catalyst(s) and product(s) from the reaction mixture and because of the possibility of operating the reaction continuously [1]. A major problem in the use of heterogeneous catalysis is the difficulty of effective interaction between a water-immiscible substrate(s) and catalyst particles owing to their hydrophilicity, which hinders the contact with hydrophobic compounds in the organic phase. Recently, we have devel-
oped a novel method for partial modification of the external surfaces of zeolite particles with alkylsilyl groups [2-4]. The particles could be assembled at a liquid-liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic compounds and act as an efficient catalyst for epoxidation of 1-octene without stirring or addition of a co-solvent. The reaction system has thus been named phase boundary catalysis (PBC). In the present study, we show some of new findings of PBC for alkene epoxidation to clarify the effective location of active titanium (Ti) sites in the catalyst.

2. EXPERIMENTAL

NaY zeolite (JRC-Z-Y5.5) was supplied as a reference catalyst from the Catalysis Society of Japan and used as received. Titanium(IV) tetra-2-propoxide (Ti(OPr)₄, 500 µmol) dissolved in 20 cm³ of benzene was added to 1.0 g of NaY, and the suspension was stirred at room temperature in open air until the benzene had almost completely evaporated. The resulting powder was then heated at 383 K overnight (w-Ti-NaY). Crystalline microporous titanium silicate, TS-1, was prepared according to the previously described procedure [5] and was designated w-TS-1. Bimodal particles partially covered with alkylsilyl groups on their external surfaces were prepared as follows (Fig. 1). To 1 g of w-Ti-NaY or w-TS-1, 0.5 cm³ of water to be absorbed by the particles was added, and the mixture was stirred until the added water soaked uniformly into the particles. The thus-obtained w-Ti-NaY or w-TS-1 aggregates were suspended in a toluene solution containing 500 µmol of octadecyl-trichlorosilane (ODS). After shaking the mixtures for ca. 5 min at room temperature, the suspensions were centrifuged to remove unreacted ODS, and the precipitates were dried at 383 K overnight. The as-prepared particles were labeled w/o-Ti-NaY and w/o-TS-1, respectively. Alkylsilyl-covered Ti-NaY and TS-1 catalysts without addition of water before the ODS treatment were also prepared and labeled o-Ti-NaY and o-TS-1, respectively. Epoxidation of 1-octene with hydrogen peroxide was performed as follows. The modified catalysts (50 mg), 1-octene (4 cm³), and 30% of aqueous H₂O₂ (1 cm³) were placed in a glass tube and reacted for 20 h at room temperature. In some experiments, the mixtures were stirred magnetically. Reaction products were analyzed by GC equipped with a DB-1 column and an FID detector.

Fig. 1 Schematic representation of the procedure for site-selective loading of alkylsilane on Ti-NaY or TS-1 particles.
3. RESULTS AND DISCUSSION

Table 1 summarizes the yields of 1,2-epoxyoctane and turnover number (TON) per Ti atom in epoxidation of 1-octene with aqueous H\textsubscript{2}O\textsubscript{2} using unmodified and modified Ti-NaY at room temperature. When the reaction was operated under the condition of vigorous stirring, all of the modified NaY catalysts showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane. Small amounts of expected by-products, such as 1-octanol or 1,2-octanediol, were also detected. The catalyst partly covered with alkylsilyl groups (w/o-Ti-NaY) showed highest activity among the catalysts examined. Under the condition of no stirring, w-Ti-NaY showed almost no activity; the epoxide yield was much lower than that obtained under the condition of vigorous stirring. Similar behavior was seen in the o-Ti-NaY system. On the other hand, it is notable that the activity of w/o-Ti-NaY seemed independent of the stirring rate, i.e., this catalyst does not require the formation of a W/O emulsion by stirring. This characteristic behavior of w/o-Ti-NaY particles might be attributed to the bimodal feature of each particle, i.e., each w/o-Ti-NaY particle has both hydrophilic and hydrophobic faces that induce affinity for both hydrophobic and hydrophilic compounds and continuous supply of reagents from both organic and aqueous phases without any enforced manipulation such as stirring in order to drive liquid-liquid mass transfer [3,4].

Figure 2 shows the results of epoxidation of 1-octene at room temperature on TS-1 systems. As was observed in the Ti-NaY system, 1,2-epoxyoctane was obtained as the main product with small amounts of other by-products. However, the order of catalytic activity was completely different from the Ti-NaY system; the highest activity was observed on unmodified TS-1 (w-TS-1), and modification with ODS induced a decrease in activity under the condition of stirring. Moreover, under the condition of no stirring, partial modification with alkylsilyl groups on the external surfaces of TS-1 particles to give the particles a bimodal character only slightly improved the activity compared with that of hydrophobic o-TS-1 particles being almost fully covered with alkylsilyl groups on the external surfaces.

Since the estimated molecular size of Ti(OPr\textsubscript{i})\textsubscript{4} (ca. 1.5 nm) is larger than the size of the pore entrance of NaY (0.7 nm), Ti species should attach to the external surfaces of NaY particles.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>epoxide yield / µmol</th>
<th>TON per Ti atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stirring</td>
<td>no stirring</td>
</tr>
<tr>
<td>w-Ti-NaY</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>w/o-Ti-NaY</td>
<td>27.4</td>
<td>27.0</td>
</tr>
<tr>
<td>o-Ti-NaY</td>
<td>5.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

All reactions were carried out for 20 h with 1-octene (4 cm\textsuperscript{3}) and catalyst (50 mg). The concentration of Ti was 500 µmol per one gram of NaY.
The alkylsilyl groups are attached to one side of the external surfaces of NaY particles, giving the particles a bimodal character. Thus, the hydrophilic-hydrophobic balance of active Ti sites on the external surfaces of NaY particles is thought to be controlled by the surface modification. On the other hand, in TS-1 catalysts, due to the predominant location of active Ti sites in the pore system, the surface modification might be ineffective for changing their environments. Moreover, the relatively hydrophobic character of the original TS-1 particles, which enable them to adsorb sufficient amounts of organic reagents [6], might also account for the lack of a significant effect of coverage of alkylsilyl groups on catalytic activity.

The bimodal Ti-NaY particles (w/o-Ti-NaY, Table 1) showed less than half of the activity of the original TS-1 particles (Fig. 2). One of the most probable reasons for this is the difference in the nature of active sites of Ti species, i.e., the presence of a small number of 4-coordinated Ti species, which are considered to be the active species in olefin epoxidation reactions [7,8]. Only almost unity of TON (Table 1) also suggests the presence of large amounts of aggregates that are inactive for the reaction. However, we employed a feasible process of Ti loading and did not optimize the yield of 4-coordinated Ti species in the preparation process. Further studies to clarify and control the structure of loaded Ti species for improvement and optimization of the catalytic activity of PBC are now underway.

References