PHASE-BOUNDARY CATALYSIS – A NOVEL GREEN CHEMISTRY CONCEPT FOR CATALYTIC PROCESSES*

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Abstract

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. Along this line, recently a novel concept of "phase-boundary catalysis (PBC)" has been proposed in order to utilize the immiscible liquid-liquid reaction system with solid catalysts [H. Nur et. al., Chem. Commun., (2000) 2235, J. Catal., 204 (2001) 402 and Langmuir, 17 (2001) 7976]. It was demonstrated that the PBC system required neither stirring to make an emulsion nor addition of a co-solvent to make a homogeneous solution to drive the reaction. 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. However, some basic facts about them remain unclear, such as the question as to where an effective location of the active sites of phase-boundary catalyst, the detail mechanism and structure of the catalyst. In this communication, the strategy for the development of this catalytic system is discussed.

Keywords: Phase-boundary catalysis; heterogeneous catalysis

Introduction

My major common interest focuses on design and preparation of a novel catalyst which can effectively works at liquid-liquid phase-boundary. The area of interest relates to liquid phase oxidation and photocatalytic reactions systems. This report will be limited to a description of my research on liquid-liquid phase-oxidation.

Nowaday, catalysts play a major role in establishing the economic strength of the chemical industry. However, increasingly demanding the clean technology in the industry, there is a need to provide new opportunities for catalysis and catalytic processes. Some of the major goals are to utilize the environmental friendly substrate, to maximize the use starting materials, to replace stoichiometric reagents with catalysts and facilitate easy separation of the final reaction mixture including the efficient recovery of catalyst. Along this line, utilization of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) as an oxidant for organic substrates has received much attention in recent years because of its environmental implication; it gives only water as a product in a wide range of oxidation

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reactions. Moreover, it is less expensive and more accessible than the other oxidizing agents, such as organic peracids or hydroperoxides. However, $\text{H}_2\text{O}_2$ 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. In this research work, we propose a novel integrated chemical system, which we have named “phase-boundary catalysis” (PBC), using aqueous $\text{H}_2\text{O}_2$ for the oxidation of organic compounds without any co-solvent [1-3]. For this system, a particulate zeolite catalyst has been designed and prepared in order to be placed at the phase boundary between aqueous $\text{H}_2\text{O}_2$ and an organic substrate.

**Experimental**

Sodium zeolite Y (NaY) supplied from the Catalysis Society of Japan (JRC-Z-Y5.5) was used as received. Partially modified NaY (w/o-Ti-NaY), whose external surface was partly covered with alkylsilane, was prepared in two steps. First, titanium oxide was loaded on the whole external surface of NaY by impregnation as follows. Titanium(IV) tetra-2-propoxide (0.142 g; 500 µmol, Wako Pure Chemical) dissolved in 20 cm$^3$ of benzene (dried with molecular sieve 4A) was added to 1.0 g of NaY powder and the suspension was stirred at room temperature in open air until the benzene was evaporated. Then the resulting powder was heated at 383 K overnight. This modified zeolite is called w-Ti-NaY. The molar amount of Ti was 500 µmol g$^{-1}$. In the second step, 1.0 g of w-Ti-NaY was grounded with 0.5 g of water in an agate mortar. To this mixture 10 cm$^3$ of toluene containing 500 µmol of octadecyltrichlorosilane (OTS, ShinEtsu) was added and the resulting suspension was vigorously shaken for ca. 5 min at ambient temperature. Then, the suspension was centrifuged to remove unreacted OTS, washed with CCl$_4$ (50 cm$^3$) and ethanol (50 cm$^3$), and dried at 383 K overnight. The modified sample was labeled w/o-Ti-NaY.

A similar procedure was also carried out for the preparation of fully modified Ti-NaY (o-Ti-NaY) without addition of water in the second step. In typical experiment, OTS (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 ethanol, and dried at 383 K overnight.

Epoxidation of 1-octene was carried out using the above catalysts. Typically, 1-octene (4 cm$^3$, Kanto Chemical), 30% aqueous $\text{H}_2\text{O}_2$ (1 cm$^3$, Wako Pure Chemicals), 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. The reaction products were analyzed by gas chromatography (Shimadzu GC-14B with an FID and a PEG 1000 column).

For characterization of the surface structures of these particles by fluorescence microscopy, fluorescein isothiocyanate (FTIC) was attached to the hydrophilic part of surfaces of these particles. Fluorescence microscopic observation was performed at room temperature using fluorescence microscope (Olympus BHT-RFK) and CCD camera (BITRAN BS-30L).
Results and discussion

Figure 1 shows the apparent distribution of modified Ti-NaY catalysts suspended in an aqueous H$_2$O$_2$ (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. 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. For all catalysts used here, 1,2-epoxyoctane was obtained as a sole detectable product. Modification of Ti-NaY by the alkylsilane led to significant rate enhancement. Especially, partial modification by alkylsilane (w/o-Ti-NaY) showed activity relatively higher than that of o-Ti-NaY, as shown in Fig. 2. When the reaction was performed under static conditions, no change in the yield of 1,2-epoxyoctane was observed on w/o-Ti-NaY, indicating that mass transfer was not rate limiting in the system containing w/o-Ti-NaY. This is the best feature of the phase-boundary catalyst compared to w-Ti-NaY and o-Ti-NaY.

Figure 3 shows representative fluorescence and optical microscopic images of particles fully covered with the dye molecules (FD-NaY) and that of w/o-NaY partly covered with them (FD-w/o-NaY). It has been clarified the amphiphilic surface structure of the modified NaY particles used in PBC systems, one side being hydrophilic and the other hydrophobic.

![Fig. 1 The apparent distribution of modified Ti-NaY in the mixture of aqueous and organic phases.](image)

From the above results, it is reasonable to conclude that during the reaction in PBC, the w/o-Ti-NaY particles are spontaneously located at the liquid-liquid phase-boundary in an aqueous-organic mixture, facing the hydrophobic alkylsilylated surface to the organic phase and hydrophilic side to the aqueous phase. In this situation, both 1-octene and H$_2$O$_2$ can be continuously supplied through the hydrophobic and hydrophilic surface of w/o-Ti-NaY, resulting in achievement of efficient catalysis even without stirring of the mixture.
Fig. 2 The yield of 1,2-epoxyoctane under stirring and static conditions. All reactions were carried out at room temperature for 20 h: 50 mg catalyst; 1-octene (4 cm$^3$) and 30% aqueous H$_2$O$_2$ (1 cm$^3$).

Fig. 3 Fluorescence and optical micrographs of fluorescent dye-modified NaY’s: (a) FD-NaY, (b) FD-w/o-NaY. Outlines are shown for comparison.
Conclusion and future works

It was clearly showed that the w/o-Ti-NaY, an amphiphilic particles having active sites (Ti-species), lie at the W/O interphase to catalyze the alkene epoxidation without stirring or the addition of a co-solvent to drive the liquid-liquid phase transfer. However, the mechanism of the phase-boundary catalysis and the structure of the catalyst are not fully understood. The future works is to improve the scientific basis for the development of novel “phase-boundary catalysis” concept, i.e., for elucidating where the reaction proceed in this system.

The development of phase-boundary catalyst will involve:

- Optimization of the phase-boundary catalyst to achieve an optimum activity and selectivity for the oxidation reaction.
- Investigation the mechanism of the phase-boundary catalysis, as well as the physichochemical properties of the catalyst (and/or active sites).
- Introduction at the different active sites on the above system and comparative investigation of these new catalysts by using a different kind of substrate and the reactions (e.g. hydrolysis [4], hydroxylation and esterification).
- Application of phase-boundary catalytic system for photocatalysis. In this system, the reaction is induced by light, and termed as Phase-boundary photocatalytic system [5].
- Application of phase-boundary catalysis for liquid-gas system [6].

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