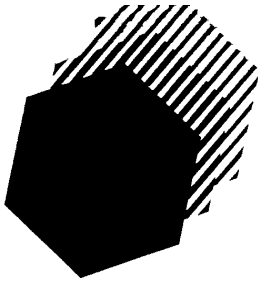

C&FC2001

Catalysis and Fine Chemicals 2001

INTERNATIONAL SYMPOSIUM ON CATALYSIS AND FINE CHEMICALS 2001

Waseda University

Tokyo, Japan

March 12-14, 2001

Book of Abstracts

Phase-boundary catalysis: a novel approach for alkene epoxidation by amphiphilic zeolite catalyst

Shigeru Ikeda, Hadi Nuir, and Bunsho Ohtani*
Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

Introduction

A novel integrated chemical system, named as phase-boundary catalysis,[1] using aqueous H_2O_2 for the oxidation of organic compounds without any co-solvent was proposed.

Experimental

Titanium(IV) tetra-2-propoxide ($Ti(OPri)_4$) was impregnated from its benzene solution to NaY zeolite powder (JRC-Z-Y5.5) and heated at 383 K overnight (W-Ti-NaY), and then n-octadecyltrichlorosilane (OTS) in toluene was impregnated to the W-Ti-NaY powder containing water (0.5 cm^3 per 1.0 g of NaY) and heated at 383 K overnight. Addition of small amount of water led to aggregation by the capillary force of water between the hydrophilic W-Ti-NaY particles. Under these conditions, only the outer surface of aggregates, being in contact with the organic phase can be modified with OTS, and 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 was labeled W/O-Ti-NaY. Fully modified Ti-NaY (O-Ti-NaY), prepared without the addition of water in the above second step, is feasibly suspended in an organic solvent.

1-Octene was used as a substrate for epoxidation reaction. Typically, 1-octene (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.

Results and Discussion

All of the modified zeolites showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane. NaY modified by Ti-species only (W-Ti-NaY) showed appreciable epoxidation ability only under vigorous stirring, i.e., in the W/O emulsion, but was negligibly active without stirring. A similar behavior was seen for the O-Ti-NaY system in which epoxide yield under static conditions was almost half to that of the stirred reaction mixture. One of the most striking features of W/O-Ti-NaY is that the partial alkylsilane modification not only enhanced the epoxidation but also changed the mode of reaction. 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. The amphiphilic nature of W/O-Ti-NaY, enabling it to lie just at the W/O phase boundary, may account for the constant activity. Therefore, the rate of this phase-boundary catalysis depends only on apparent area of W/O interface. In fact, when a narrow-bore reaction tube was used to decrease the apparent interface area, the activity was reduced as expected.

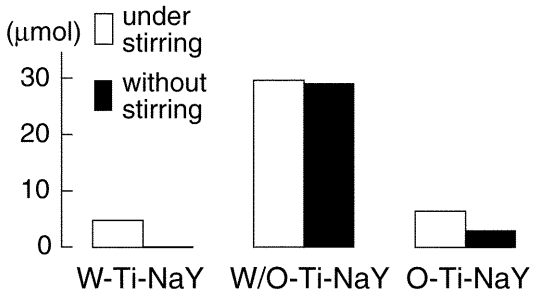

Fig 1. Effect of stirring on the formation of 1,2 epoxyoctane.

Reference

1. H. Nur, S. Ikeda, and B. Ohtani, *Chem. Commum.* (2000) 2235-2236.