

Symposium
Frontiers of Nano-scale Catalysis and
Electrochemistry

– Proposals for the Research in the 21st Century –
In Commemoration of Centennial Birthday of
Professor Juro Horiuti

(CES21)

March 19 ~ 21, 2001

Sapporo Japan

Organized by
Organizing Committee of CES21 and Co-organized by
Catalysis Research Center, Hokkaido University

Sponsored by
Hokkaido Branches of Chemical Society of Japan,
Electrochemical Society of Japan, and Catalysis Society of Japan
Division of Electrocatalysis and Photocatalysis, Catalysis Society of Japan
Hokkaido Prefecture and City of Sapporo

Liquid-liquid phase-boundary catalysis by amphiphilic zeolite nanoparticles

Shigeru Ikeda, Hadi Nur, and Bunsho Ohtani

Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

Introduction

A novel catalytic epoxidation system, named phase-boundary catalysis,¹ using amphiphilic zeolite nanoparticles and aqueous H₂O₂ without any co-solvent is 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) was impregnated from toluene to the w-Ti-NaY powder containing water (0.5 cm³ per 1.0 g of NaY) followed by heating at 383 K overnight. Addition of small amount of water led to aggregation of the hydrophilic w-Ti-NaY particles induced by capillary force of water between the particles. Under these conditions, only the outer surface of aggregates, 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 (figure 1). 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 H₂O₂ (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 with 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. Similar behavior was seen for the o-Ti-NaY system in which epoxide yield under static conditions was almost half of that under stirring. 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.

Reference

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

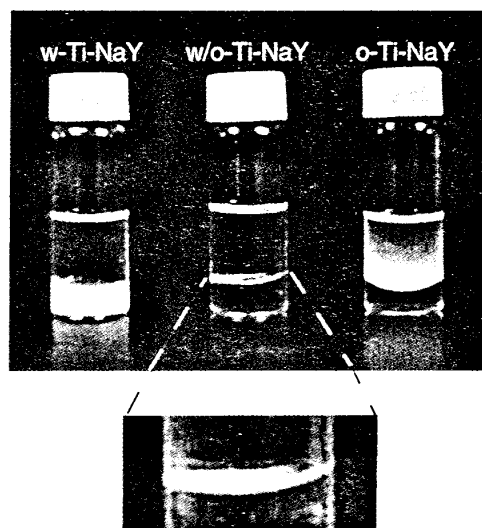


Fig 1. Photographs of w-Ti-NaY, w/o-Ti-NaY, and o-Ti-NaY suspended in 1-octene (4 ml) - water (1 ml) solution.