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**AMPHIPHILIC NaY ZEOLITE PARTICLES LOADED WITH NIOBIC
ACID: MATERIALS WITH APPLICATIONS FOR CATALYSIS IN
IMMISCIBLE LIQUID-LIQUID SYSTEM**

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Abstract

The catalytic potential of catalysts for acid-catalyzed reactions has been demonstrated by NaY zeolite loaded with alkylsilane-covered niobic acid in the liquid phase hydration of 1,2-epoxyoctane with water. The catalytic activity of the catalysts was correlated to the amphiphilic character of the solid catalyst particles.

Keywords: Amphiphilic zeolite particles, acid-catalyzed reactions

INTRODUCTION

The fast-growing insight into green chemistry has led to research more focused on the area of environmentally benign catalysts [1, 2]. Along this line, we recently reported a new approach to modify the surface of zeolite, resulting hydrophilic and hydrophobic regions, for application as catalyst in immiscible liquid-liquid systems in co-solvent free condition [3-6]. The organic transformations under solvent-free conditions are attracting increasing attention because the use of large quantities of organic solvents is not only

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detrimental to the environment but also economically unfavorable. The proposed model of a catalyst for immiscible liquid-liquid reactions is depicted in Fig. 1. Previously, we reported a zeolite loaded with alkylsilane-covered titanium oxide as catalyst for the oxidation of alkenes using aqueous H_2O_2 . In this paper, the study is now extended to acid catalysis in which the hydration of 1,2-epoxyoctane using NaY zeolite loaded with niobic acid-covered alkylsilane is chosen as a model catalytic system. It has been reported that the surface acid strength of niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) corresponds to the acid strength of 70% sulfuric acid and exhibits high stability for acid catalyzed reactions in which water molecules participate [7]. Here, we demonstrate that the catalytic activity of the modified zeolite can be attributed to the amphiphilic character of the solid particles.

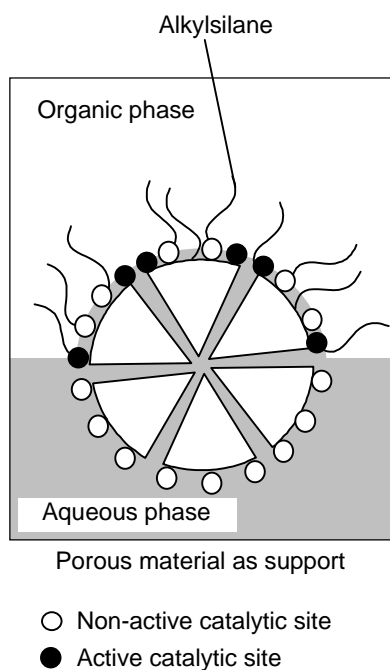


Fig. 1. Proposed model of catalyst for immiscible liquid-liquid reactions

EXPERIMENTAL

NaY zeolite (JRC-Z-Y5.5) with a primary particle diameter quoted as *ca.* 500 nm was supplied by the Catalysis Society of Japan and used as received. NaY zeolite loaded with niobic acid (Nb-NaY) was prepared by impregnation of niobium pentaethoxide ($\text{Nb}(\text{OC}_2\text{H}_5)_5$) from its ethanol solution at room

temperature. Then, the solid was heated at 130°C overnight. The molar amount of Nb was 500 $\mu\text{mol g}^{-1}$ zeolite. Unmodified Nb-NaY is labeled as w-Nb-NaY. Modified Nb-NaY, on which the external surface was covered partly with alkylsilane, was prepared by attachment of *n*-octadecyltrichlorosilane (ODS). This preparation method is similar to those given in our recent papers [3-6]. In a typical experiment, in order to modify w-Nb-NaY with alkylsilane, the w-Nb-NaY powder containing water (0.5 g per 1.0 g of w-Nb-NaY) was immersed in 5 mL of toluene containing 500 μmol of *n*-octadecyltrichlorosilane (ODS, ShinEtsu) and the suspension was shaken for *ca.* 5 min at room temperature. Then the solid was collected by centrifuging and dried at 110°C for 5 h. Due to the hydrophilicity of the w-Nb-NaY surface, addition of a small amount of water 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 which, is in contact with the organic phase can be modified with ODS. The partly modified sample was labeled as w/o-Nb-NaY. Fully modified Nb-NaY (o-Nb-NaY) was prepared without addition of water.

Hydration of 1,2-epoxyoctane with water was carried out at 70°C. In detail, 1,2-epoxyoctane (1 mL), water (1 mL) and catalyst powder (25 mg) were placed in a glass tube, and the reaction was performed at 70°C with stirring (*ca.* 1000 rpm) after removal of oxygen by argon bubbling. The reaction products were analyzed by gas chromatography (Shimadzu GC-14B with FID and DB-1 column) and GC/MS.

The photograph of the emulsion formed in the presence of modified NaY zeolite particles was taken under an optical microscope. Before the photograph was taken, the mixture was stirred vigorously at *ca.* 1000 rpm. Methylene blue (dissolved in aqueous phase) was used as an indicator in order to clarify the type of the emulsion, either oil in water (o/w) or water in oil (w/o).

RESULTS AND DISCUSSION

Figure 2 shows the rate of the formation of 1,2-octanediol in the mixture of 1,2-epoxyoctane and water in the presence of modified Nb-NaY catalysts. It confirms that the hydration of epoxyoctane is more efficiently catalyzed by w/o-Nb-NaY than both w-Nb-NaY and o-Nb-NaY. In order to rationalize the activities in hydration of 1,2-epoxyoctane, one should consider the formation of emulsion, because in this form the specific interfacial interactions between the solid catalyst surface and the two immiscible liquid phases increase the surface contact (wettability) of the catalyst with the reactants. For maximum efficiency, the catalyst should be wetted preferentially by the two liquid phases. If the solid particles are too strongly wetted by either of the two liquid phases

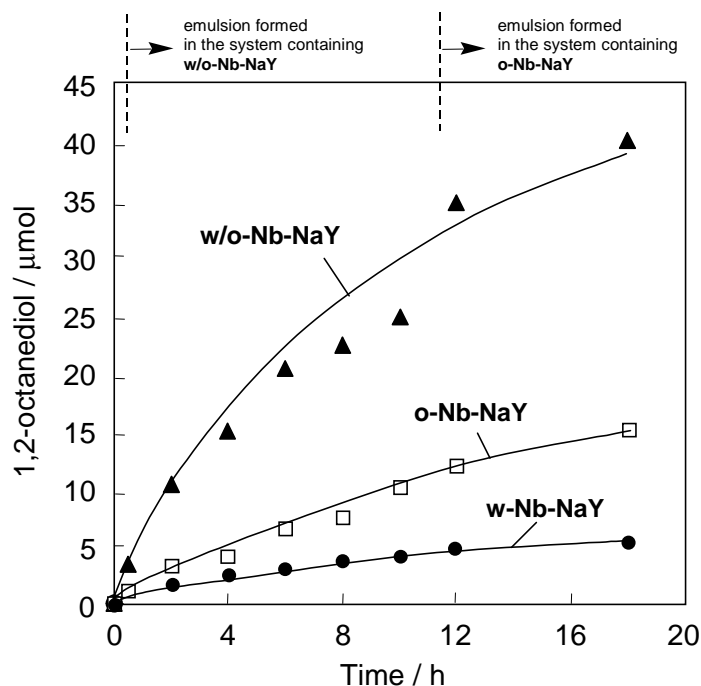


Fig. 2. The yield of 1,2-octanediol in organic and aqueous phases for the hydration of 1,2-epoxyoctane using various modified Nb-NaY under stirring conditions. All reactions were carried out at 70°C: 25 mg catalyst; 1 mL 1,2-epoxyoctane and 1 mL water

the required stabilizing action will not result [8]. Based on these considerations, the formation of the emulsion in the presence of the solid particles was examined. It was observed that, after *ca.* 30 min of reaction, an emulsion was formed in the system containing w/o-Nb-NaY, whereas o-Nb-NaY was still located at the organic phase due to its hydrophobic nature. Instead, w-Nb-NaY was distinctly well dispersed in the aqueous phase. After *ca.* 10 h of reaction, an emulsion was also formed in the system containing o-Nb-NaY. As is shown in Fig. 3, it is clearly demonstrated that an emulsion has been formed, resulting in an abrupt visual homogenization. No emulsion was formed in the system containing w-Nb-NaY.

If the surface structure of w/o-Nb-NaY has a good hydrophile-liphophile balance, one expects that the two immiscible liquids can be stabilized for a long period of time. Figure 4 shows the optical microscope photographs of the type of emulsion formed; the w/o-Nb-NaY and o-Nb-NaY act as emulsifier to

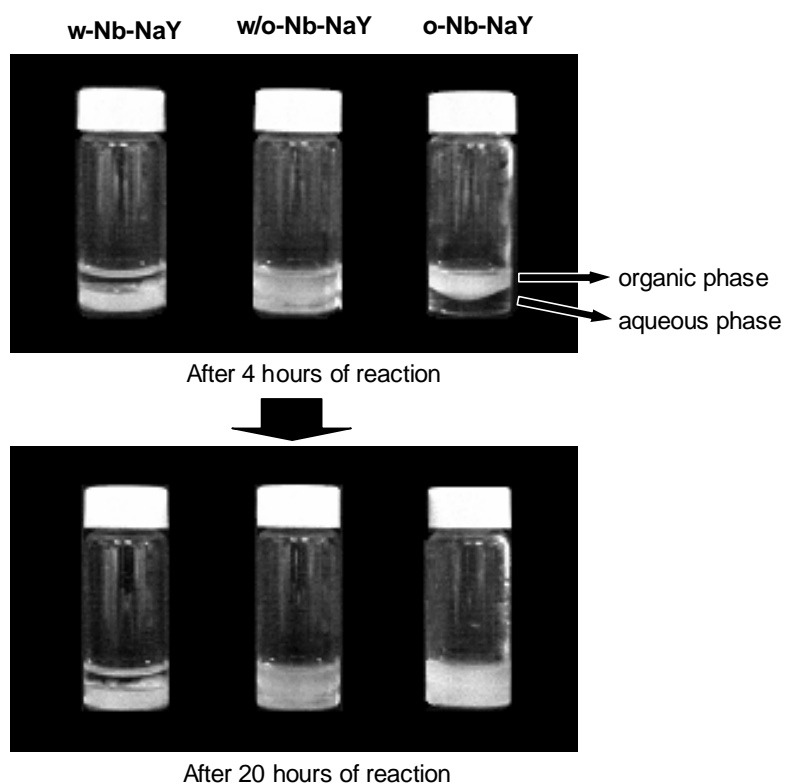


Fig. 3. The photograph shows the distribution of solid catalyst after 4 and 20 h of reaction of the reaction shown in Fig. 2

stabilize the 1,2-epoxyoctane and water mixture in the form of w/o type of emulsion. Interestingly, the emulsion can be stabilized by w/o-Nb-NaY for up to 24 h, whereas stability of emulsion for the system containing o-Nb-NaY was only 1 hour. This suggests that w/o-Nb-NaY possesses a good bimodal amphiphilic character to stabilize the immiscible mixture of organic and aqueous phases in order to form a relatively more stable emulsion.

All the systems containing modified niobic acid functionalized zeolites (w-Nb-NaY, w/o-Nb-NaY and o-Nb-NaY) produced 1,2-octanediol as the major product (Fig. 2). The w/o-Nb-NaY gave the highest yield of diol compared to those of w-Nb-NaY and o-Nb-NaY. It is possible that the hydrophilic and hydrophobic regions of w/o-Nb-NaY play an important role in the eventual formation of the diol by supplying continuously the organic and aqueous substrates to the active sites.

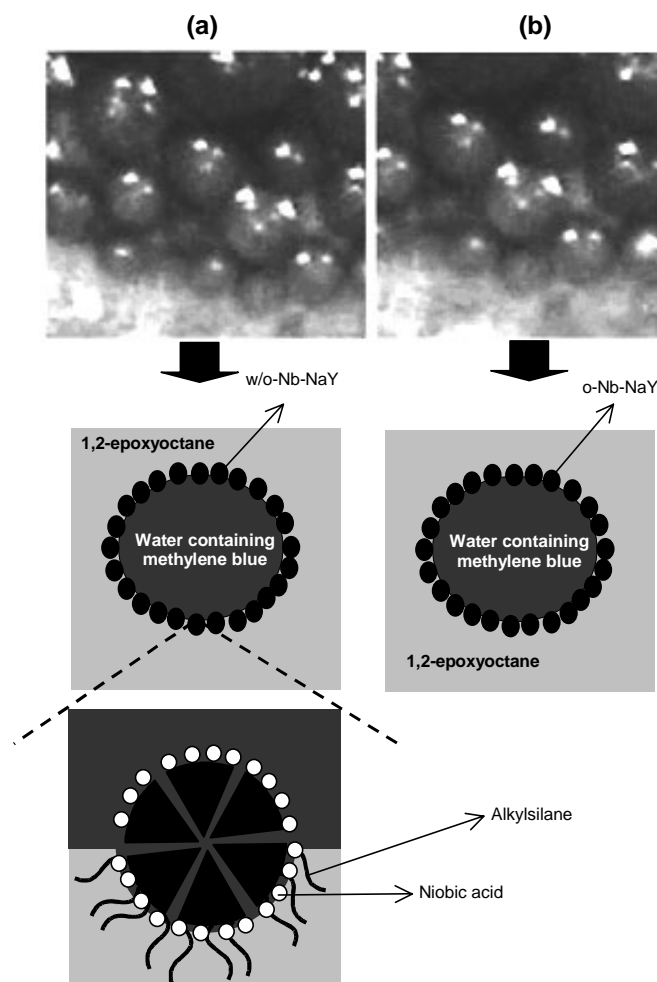


Fig. 4. Photographs of water in oil (w/o) emulsion stabilized by (a) w/o-Nb-NaY (b) o-Nb-NaY. Photographs were taken from the emulsion after 20 hours under stirring conditions

Although experimental evidence is not yet available at this stage, the Nb active sites and alkylosilyl groups should be attached to the external surface of NaY since the estimated molecular size of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ (*ca.* 0.90 nm), the source of Nb sites, and alkylosilane (*ca.* 0.5 nm x 2.6 nm), the source of alkylosilyl, are larger than the size of the pore-entrance of NaY (*ca.* 0.70 nm). Based on these data, there is a possibility of the alkylosilyl being attached to the

niobic acid sites, leading to a decrease in the activity of o-Nb-NaY. In order to exclude this argument, the Temperature Programmed Desorption (TPD) of preadsorbed ammonia measurements were performed on w-Nb-NaY, w/o-Nb-NaY and o-Nb-NaY. It was observed that no significant difference in the strength and amount of acid sites from the calculated amount of desorbed ammonia among the samples (data not shown). This suggests that the acid sites on the modified samples are not covered by ODS. On the basis of these results, it can be proposed that the higher activity of w/o-Nb-NaY is due to the stabilization of liquid-liquid system by bimodal amphiphilic particles as shown in Fig. 4a.

In conclusion, the results described above indicate that w/o-Nb-NaY (NaY zeolite loaded with alkylsilane-covered niobic acid) is potentially capable of catalyzing the hydration of 1,2-epoxyoctane at the interphase. The good catalytic activity could be related to the amphiphilic character of the solid particles.

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