



# Catalytic hydrolysis of hydrophobic esters on/in water by high-silica large pore zeolites



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## ABSTRACT

Hydrolysis of water-insoluble esters is an industrially important but challenging reaction, because the esters are mostly present in oil droplets on water during the reaction. On the basis of the screening results for hydrolysis of a water-insoluble ester, 3-phenylpropionate, on/in water by 25 types of heterogeneous and homogenous catalysts, we have found that H $\beta$  zeolite with a moderate Si/Al ratio (Si/Al = 75), H $\beta$ -75, is an effective and reusable catalyst for hydrolysis of hydrophobic esters. The hydrolysis of esters with different sizes is studied by H $\beta$  and HZSM5 zeolites with different Si/Al ratios, and the results show the hydrophobicity, pore size and number of Brønsted acid sites are critical factors affecting the catalytic activity for this system. Kinetic and adsorption studies show that the high yields by H $\beta$ -75 are due to preferential interaction of the hydrophobic zeolite pore with hydrophobic esters over polar molecules (carboxylic acids, water, alcohols) and transfer of the carboxylic acids to the oil droplets on water, both of which inhibit the reverse reaction (esterification of the carboxylic acids).

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## 1. Introduction

Hydrolysis of esters is a fundamental organic transformation in the synthesis of various chemicals. Conventionally, the hydrolysis of esters is carried out with homogeneous Brønsted bases such as NaOH [1], which suffers from low atom-efficiency due to the use of stoichiometric amount of the base as well as the use of stoichiometric amount of acids to isolate the carboxylic acids in the workup. Potentially, Brønsted acids-catalyzed hydrolysis of esters can offer a greener route to carboxylic acids. Generally, esters are less hydrophilic than the corresponding carboxylic acids and alcohols. In addition, conventional homogeneous Brønsted acid catalysts are soluble in water. Hence, homogeneous Brønsted acid catalysts can promote the reverse esterification of carboxylic acids and alcohols in water, which can result in low yields of the carboxylic acids and alcohols for the Brønsted acid-catalyzed hydrolysis of water-insoluble esters. Heterogeneous Brønsted acid catalysts with a relatively hydrophobic nature [2,3], including zeolites with a high Si/Al ratio [2–4], salts of heteropoly acid [2,3,5–9], metal oxides [10] and acidic resins [11] have been shown to catalyze the hydrolysis of esters in water. The hydrophobic surface or pore of the water-tolerant solid Brønsted acid catalysts will

interact preferentially with the esters over hydrophilic products (carboxylic acids and alcohols), and thus, they will be promising catalysts for hydrolysis of esters in water. However, most of the previous reports [2–11] of the hydrophobic solid acid-catalyzed hydrolysis of esters tested only hydrophilic esters (mostly ethyl acetate), and the activity of the solid catalysts was lower than the conventional Brønsted acids. For example, Okuhara et al. [6] compared the activity of various acid catalysts for hydrolysis of ethyl acetate in water and showed that sulfonic acid (H<sub>2</sub>SO<sub>4</sub>) and *p*-toluenesulfonic acid (PTSA) showed more than 10 times higher reaction rates (per weight of the catalyst) than hydrophobic solid acids, including zeolites, heteropoly acids, metal oxides and acidic resins. Contrary to the water-soluble ester (ethyl acetate), water-insoluble esters are mostly present at oil droplets on water, and hence, the solid catalyst suspended in water cannot be effective for hydrolysis of the water-insoluble esters. In nature, an enzyme named carboxylesterase or carboxylic-ester hydrolase catalyzes hydrolysis of hydrophobic esters in water [12]. The active site of this enzyme is located at the bottom of a hydrophobic narrow tunnel [12]. As for artificial catalysts, to our knowledge, only two methods have been reported to show high yields for the hydrolysis of water-insoluble esters in the presence of excess amount of water, and both of the systems adopt Brønsted acid sites at hydrophobic environments [13–15]. One successful example is *N,N*-diarylammonium pyrosulfate catalyst reported by Ishihara et al. [13] In the presence of excess amount of water, the

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homogeneous Brønsted acid catalyst forms reverse micelle in organic layer to promote the hydrolysis of hydrophobic esters on the surface of the oil-in-water emulsion, resulting in high conversions for various hydrophobic esters [13]. However, the method has drawbacks of difficulties in catalyst/products separation and catalyst reuse. Another example is an octadecylsilane-treated HZSM5 zeolite [14,15] as a water-tolerant heterogeneous Brønsted acid catalyst. The immobilization of the alkyl-group on the outer surface of zeolites increases the hydrophobicity of the zeolites [16–18] and hence increases the catalytic activity of HZSM5 for hydrolysis of the esters [14,15]. However, the method suffers from serious drawbacks of limited substrate scope due to a narrow pore size of HZSM5, necessity of toluene as a co-solvent and no report of catalyst reuse.

It is well established that aluminosilicate zeolites with a high Si/Al ratio, so-called high-silica zeolites, have high hydrophobicity due to nonpolar nature of the Si-O-Si surface [3,4,19–21]. Among various commercially available zeolites, proton-exchanged  $\beta$ -BEA zeolite (H $\beta$ ) has relatively large pore size and three-dimensional pore structure, which allow rapid diffusion of bulky organic substrates and products. The strong Brønsted acid sites in the hydrophobic pore of H $\beta$  will be effective for acid-catalyzed reactions of hydrophobic substrates. Recently, high-silica H $\beta$  zeolites have been shown to catalyze organic transformations in the presence of water [22,23]. We hypothesized that hydrophobic and large pore H $\beta$  zeolites may be effective for the catalytic hydrolysis of hydrophobic esters in the presence of excess amount of water. We report herein that a high-silica H $\beta$  zeolite shows higher activity than conventional homogeneous acid catalysts and the water-tolerant Brønsted [3] and Lewis [24–26] acid catalysts for hydrolysis of hydrophobic esters in the presence of excess amount of water. Catalytic results show catalyst reusability and wide applicability of this method. To study critical factors affecting the catalytic activity, fundamental studies are also carried out for H $\beta$  and HZSM5 zeolites with different Si/Al ratio and alkyl-group immobilized H $\beta$ .

## 2. Experimental

### 2.1. General

Commercially available organic compounds (from Tokyo Chemical Industry or Aldrich) were used without further purification. GC (Shimadzu GC-2014) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY<sup>+</sup>-1 capillary column (Frontier Laboratories Ltd.) with N<sub>2</sub> and He as the carrier. Column chromatography was performed with silica gel 60 (spherical, 63–210  $\mu$ m, Kanto Chemical Co. Ltd.). Molecular sieves 4 Å (MS4Å) were dehydrated at 100 °C.

### 2.2. Catalyst preparation

The zeolites used in this study are designated as H $\beta$ -*x*, where *x* denotes the Si/Al ratio of the H $\beta$  zeolite. H $\beta$ -75 (JRC-Z-HB150, originally supplied from Clariant), HZSM5-45 (JRC-Z5-90H(1)), HMOR-45 (JRC-Z-HM90, originally supplied from Clariant), TiO<sub>2</sub> (JRC-TIO-4), CeO<sub>2</sub> (JRC-CEO-3), amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (JRC-SAL-2, Al<sub>2</sub>O<sub>3</sub> content = 13.75 wt%, surface area = 560 m<sup>2</sup> g<sup>-1</sup>) were supplied from Catalysis Society of Japan. H $\beta$ -20 (HSZ-940HOA), H $\beta$ -255 (HSZ-980HOA), HZSM5-20 (HSZ-840HOA) and HY-50 (HSZ-385HUA) were commercially purchased from Tosoh Co. HZSM5-75 and HZSM5-300 were supplied from N.E. CHEMCAT Co. Niobic acid (HY-340) was kindly supplied by CBMM, and Nb<sub>2</sub>O<sub>5</sub> was prepared by calcination of the niobic acid at 500 °C for 3 h. SiO<sub>2</sub> (Q-10) was supplied from Fuji Silysia Chemical Ltd.

ZrO<sub>2</sub> and SnO<sub>2</sub> were prepared by calcination (500 °C, 3 h) of ZrO<sub>2</sub>·*n*H<sub>2</sub>O and H<sub>2</sub>SnO<sub>3</sub> (Kojundo Chemical Laboratory Co., Ltd.). Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> was prepared by titrating H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Nippon Inorganic Color and Chemicals Co.) by aqueous solution of Cs<sub>2</sub>CO<sub>3</sub> (0.10 mol dm<sup>-3</sup>) with vigorous stirring, followed by centrifuging and drying at 200 °C. Montmorillonite K10 clay and sulfonic resins (Amberlyst-15 and Nafion-SiO<sub>2</sub> composite) were purchased from Sigma-Aldrich. Scandium(III) trifluoromethanesulfonate, Sc(OTf)<sub>3</sub>, and *p*-toluenesulfonic acid (PTSA) were purchased from Tokyo Chemical Industry.

Octadecyltriethoxysilane-treated H $\beta$ -20 (OD-H $\beta$ -20) was prepared by refluxing a mixture of the H $\beta$ -20 (1 g, dried at 100 °C) and octadecyltriethoxysilane (0.2 mmol) in dry toluene (5 mL) for 6 h, followed by filtering and washing with toluene and acetone, and by drying at 100 °C for 1 h. The number of the octadecyl-groups determined by the CO<sub>2</sub> formation in the temperature programmed oxidation analysis (25–500 °C under O<sub>2</sub> flow) was 0.09 mmol g<sup>-1</sup>.

### 2.3. In situ IR

The pyridine-adsorption IR (infrared) study was carried with JASCO FT/IR-4200 spectrometer equipped with an MCT detector using a flow-type IR cell connected to a flow reaction system. The IR disk of the sample (40 mg, 20 mm  $\phi$ ) was first dehydrated under He flow at 500 °C, and then a background spectrum was taken under He flow at 200 °C. Then, pyridine (0.3 mmol g<sup>-1</sup>) was introduced to the sample, followed by purging by He for 600 s, and by IR measurement of adsorbed pyridine at 200 °C.

### 2.4. Catalytic tests

The heterogeneous catalysts, stored under ambient conditions, were used for catalytic reactions without any pretreatment. Typically, ester (1 mmol), 1 mL H<sub>2</sub>O and 10 mg of catalysts and a magnetic starter bar were added to a reaction vessel (Pyrex pressure tube, 13 mL), and the mixture was heated at 130 °C under air with stirring at 300 rpm. For the catalytic tests in Table 1 and kinetic study, conversions and yields were determined by GC-FID using *n*-dodecane as an internal standard as follows. After completion of the reaction, acetone (7 mL) was added to the mixture, and the catalyst was separated by centrifugation. Then, *n*-dodecane (0.2 mmol) was added to the reaction mixture, and the mixture was analyzed by GC-FID and GC-MS. The GC-FID sensitivities of the products were determined using commercial carboxylic acids or the isolated products after the reaction. For some of the products in Tables 2 and 3, we determined isolated yields of the carboxylic acids as follows. After the filtration of the catalyst, followed by washing the catalyst with acetone (6 mL), and by evaporation, the product was isolated by column chromatography using silica gel 60 (spherical, 63–210  $\mu$ m, Kanto Chemical Co. Ltd.) with hexane/ethyl acetate (60/40–80/20) as the eluting solvent, followed by analyses by <sup>1</sup>H NMR, <sup>13</sup>C NMR and GC-MS equipped with the same column as GC-FID.

### 2.5. Adsorption experiments

Liquid phase adsorption experiments (Figs. 7, 10 and 1) were carried out as follows. Organic molecules (1 mmol of 1-pentanol, methyl 3-phenylpropionate, ethyl acetate and acetic acid) with 1 mL water were stirred with solid adsorbent (0.1 g) for 24 h at room temperature, followed by centrifugation to separate the solids from the liquid. Then, acetone (6 mL) and the internal standard (0.2 mmol *n*-dodecane) were added to the liquid, which was analyzed by GC-FID.

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