Effect of water properties on selectivity for 1-octene and 2-octanol reaction systems in sub- and supercritical water using a TiO$_2$ catalyst

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ABSTRACT

The effect of water properties on solid acid catalysis using TiO$_2$ as the catalyst in sub- and supercritical water was elucidated using the reactions of 1-octene and 2-octanol as models. Kinetic data for these reactions at 290–410 °C and 25 MPa were analyzed, and relationships between reaction selectivities and water properties were evaluated quantitatively. The *cis/trans* selectivity for 2-octene produced in reactions of both 1-octene and 2-octanol drastically increased at around the critical temperature of water, and was quantitatively explained using the model of acid catalysis in sub- and supercritical water derived from kinetic analyses. The hydration selectivity of 1-octene conversion had a local maximum at around 330 °C, which was explained by considering the change in reactivity of water as a reactant caused by changes in both water density and the degree of hydrogen bonding.

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1. Introduction

Sub- and supercritical water are promising media for organic reactions. The solvent properties of water drastically change with temperature and pressure [1–3], and can be utilized to control organic reactions. Due to this characteristic and low environmental load of water, sub- and supercritical water have attracted attention as the reaction media for many types of organic reaction [4–7]. Recently, heterogeneous catalysis in sub- and supercritical water has received attention [8–11], with changes in solvent properties reportedly affecting the acidity of the solid catalysts, including the amount [12] and type [13,14] of acid sites. As solid catalyst acidity strongly affects the reaction rate and selectivity, sub- and supercritical water have the potential to control solid acid-catalyzed reactions via temperature and pressure adjustments.

In a previous work, we reported that the acid-type of TiO$_2$ catalysts changed according to water properties in a model reaction with 1-octene [13]. At a low temperature and high pressure, water dissociates effectively on the catalyst surface, because its density (ρ) is high and ion product (K_W) is large; thus, the reaction is mainly catalyzed at the Brönsted acid sites. In contrast, at a high temperature and low pressure, Lewis acid sites participate in the reaction because water cannot dissociate and tends to desorb from

the catalyst surface. Based on our observation, we also made the suggestion that the change in acid type according to water properties affected the *cis/trans* ratio in the 2-octene product. However, further quantitative consideration is needed to clarify the effect of water properties on reaction selectivity by changing the acid-type. Furthermore, previous reports have suggested that water acts not only as a reaction medium, but also as a reactant during some reactions in sub- and supercritical water [4,5]. In reactions with 1-octene, the starting material is consumed by both double-bond isomerization and hydration reactions, with water acting as a reactant in the latter. Therefore, the effect of changing water properties on the activity of water as a reactant can be elucidated using information about the dependence of reaction selectivity on water properties.

In order to discuss the effects of water properties on reaction selectivity, it is important to determine proper reaction rate constants for each reaction. We previously analyzed kinetic data from 1-octene reactions, and identified the contribution of water properties to reaction pathways, including isomerization of 1-octene to 2-octene (R1), hydration of 1-octene to 2-octanol (R2), and dehydration of 2-octanol to 2-octene (R3) [13]. Although overall relationships between water properties and TiO$_2$ acidity in sub- and supercritical water were successfully discussed, further kinetic data, such as for 2-octanol dehydration reactions, are needed to enable quantitative discussion of the effect of water properties on reaction selectivity. In this study, we examined reactions of 2-octanol in sub- and supercritical water using TiO$_2$ as a catalyst.

Analysis of this newly obtained data, combined with our previous data for reactions of 1-octene, allowed us to determine the effect of water properties on each reaction rate constant, and quantitatively discuss relationships between water properties and reaction selectivity. The purpose of this study was to obtain fundamental knowledge regarding the role of water in solid acid-catalyzed reactions in sub- and supercritical water, which is important for controlling reaction selectivity in acid-catalyzed reactions, via quantitative discussion about the effect of water properties on selectivity in the reactions of 1-octene and 2-octanol.

2. Materials and methods

2.1. Reagents

2-Octanol (Tokyo Chemical Industries Co., Ltd., Japan), 1-octene (Kanto Chemical Co., Inc., Japan), and *n*-pentane (Wako Pure Chemical Industries, Ltd., Japan) were used as purchased. Distilled water was prepared using an RFD240HA distillation unit (Advantec Toyo Kaisha, Ltd., Japan), and was degassed by bubbling with N_2 gas prior to use. TiO_2 powder (anatase-type, containing a small amount of rutile-type) was purchased from Wako Pure Chemical Industries, Ltd., Japan.

2.2. Catalyst preparation

The TiO_2 catalyst was prepared using the same procedure as in our previous study [13]. TiO_2 powders were shaped into a granular form (diameter, 0.50–0.71 mm), then loaded into fixed-bed reactor made of SUS316, and conditioned in supercritical water at 450 °C and 25 MPa in order to avoid changes in crystalline structure during the reaction. As previously reported, almost all TiO_2 was rutile-type with a BET surface area of 12.3 m^2/g.

2.3. Experimental procedure

Reactions with 2-octanol were conducted using a fixed-bed flow reactor made of SUS316 at 290–410 °C and 19–32 MPa. Distilled water and 2-octanol were pumped separately using two pumps (PU-980 and PU-2085; JASCO Corp., Japan, or PU-2080; JASCO Corp., Japan and 260D; Teledyne ISCO, Inc., USA), and distilled water was preheated to the reaction temperature in a preheat line. The two streams were mixed and fed into the fixed-bed reactor. The preheat line and reactor were set in either a fluidized sand bath or a heating oven. The 2-octanol concentration at the reactor entrance was 0.10 mol/dm^3. The stream emitted from the reactor was immediately cooled with a water-cooled heat exchanger, and then depressurized using a back-pressure regulator (SCF-Bpg; JASCO Corp., Japan). W/F, defined as the weight of loaded catalyst (0.18–0.64 g) divided by the volumetric flow rate in the reactor (4.2×10^{-8}–4.0×10^{-7} m^3/s), was used to indicate the reaction time. W/F was controlled both by adjusting the amount of loaded catalyst and the volumetric flow rate in the reactor.

2.4. Analysis

Organics were extracted from the effluent with *n*-pentane, and analyzed by gas chromatography equipped with a flame ionization detector (GC–14 B or GC-2014; Shimadzu Corp., Japan) equipped with capillary column (TC-1701; GL Sciences, Inc., Japan). The catalyst was characterized using X-ray diffraction (XRD; M03X HF22; Mac Science, Japan) and N_2-adsorption (Jemini 2360; Shimadzu Corp., Japan) methods.
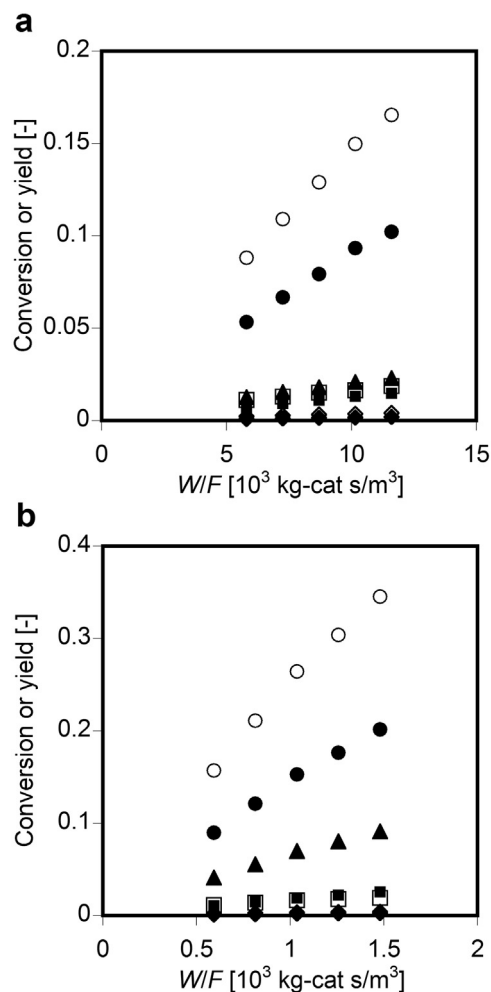
Fig. 1. Conversions (X) or yields (Y) of 2-octanol reactions at 25 MPa and (a) 330 °C and (b) 400 °C. (○) $X_{2\text{-octanol}}$, (▲) $Y_{1\text{-octene}}$, (●) $Y_{2\text{-octene}}$, (■) $Y_{3\text{-octene}}$, (♦) $Y_{4\text{-octene}}$, (□) $Y_{3\text{-octanol}}$, (◇) $Y_{4\text{-octanol}}$.

3. Results and discussion

3.1. Reaction rate and product distribution of 2-octanol reactions

Fig. 1 shows the conversions (X) and yields (Y) of 2-octanol reactions at (a) 330 °C and 25 MPa, and (b) 400 °C and 25 MPa. The main products were 2-octene (both *cis* and *trans*) and 1-octene, indicating that dehydration was the main reaction. In addition, 3-octene, 3-octanol, 4-octene, and 4-octanol were produced as byproducts, thought to be produced by isomerization and hydration reactions of 2-octene, and further reactions of the initial products from 2-octene. Reproducibility of the experiment was checked at 350 °C and 25 MPa for three times (Fig. S1 in the Supplementary material). In addition, it was confirmed that the reaction with TiO_2 catalyst was sufficiently faster than that without catalyst (Fig. S2 in the Supplementary material).

Comparing the dependences of 2-octanol and 1-octene conversion on W/F reported in the literature [13], the reaction rates of 2-octanol were at least ten-fold higher than those of 1-octene. Furthermore, the product distributions of the 2-octanol reactions indicated that 2-octanol dehydration, forming 1-octene, made the larger contribution, particularly under higher temperature conditions. Therefore, the main reactions of the 1-octene and 2-octanol reaction systems were 1-octene isomerization to 2-octene (R1), 1-octene hydration to 2-octanol (R2), 2-octanol dehydration to 1-