Effect of supercritical water on the stability of WO$_X$/TiO$_2$ and NbO$_X$/TiO$_2$ catalysts during glycerol dehydration

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ABSTRACT

The catalytic stabilities of WO$_X$/TiO$_2$ (WTi) and NbO$_X$/TiO$_2$ (NbTi) during glycerol dehydration in 400 °C supercritical water at 25 MPa and 33 MPa were investigated. The effects of coking and active component leaching on catalytic activities are quantitatively discussed. The catalytic activity of NbTi did not decrease significantly with time at both pressures. At 25 MPa, the coke precursors on the NbTi surface dissolved in the supercritical water because of the middle-strength acidity of NbTi, thus preventing loss of catalytic activities due to coking. At 33 MPa, coking was more suppressed, most likely because the coke precursors were transferred from the catalyst pores more effectively than at 25 MPa. Leaching of WO$_X$ from WTi occurred at the higher reaction pressure due to high ion products of water, but leaching of Nb from NbTi did not occur because of the high chemical stability of NbO$_X$ in acid/base solutions.

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1. Introduction

Subcritical water and supercritical water are promising reaction media for organic syntheses [1,2] and biomass conversion [3,4]. The solvent properties of water drastically change depending on temperature and pressure [5], and this can be exploited to control organic reactions. Recently, the use of solid acid catalysts for controlling reactions in sub- and supercritical water has received considerable research attention, and reactions such as the hydration of olefins [6,7] and reactions of sugars [8,9] have been investigated. The solvent properties of sub- and supercritical water affect the surface properties of solid catalysts, such as acid amount and acid type, and can cause changes in their activity and selectivity [10,11]. Therefore, solid-catalyzed reactions can be controlled in sub- and supercritical water by adjusting the temperature and the pressure.

In solid-catalyzed reactions, not only the initial activity of the catalyst but also the stability of the catalyst is important, and the causes and mechanisms of catalyst deactivation in gas phase reactions have been extensively reviewed in the literature [12,13]. In the case of solid acid catalysis, coking is one of the most important phenomena affecting catalytic stability. On solid acid catalysts, reactants and/or products are polymerized to condensed hydrocarbons. These hydrocarbons can deposit on the catalyst and cause

blockage of acid sites and/or plugging of catalyst pores. Coking has been reported to occur during various reactions, such as phenol methylation [14], fries rearrangement of phenyl acetate [15], reactions of acetone [16], and cyclodehydration of xylose to furfural [17]. In addition to coking, changes in the catalyst structure under high reaction temperatures can also lead to catalyst deactivation. The surface area of catalysts can decrease owing to crystal growth on the catalyst and/or pore collapse, and these processes are generally accelerated by the presence of water [12]. Furthermore, leaching of active components from catalysts can occur in liquid phase reactions [18]. Leaching causes the loss of acid sites in supported catalysts, and collapse of the active phase in mixed catalysts.

The presence of supercritical fluids can affect the deactivation of catalysts both positively and negatively. Supercritical carbon dioxide has been reported to dissolve coking precursors and enhance the stability of porous catalyst owing to its high density and high diffusivity [19]. Conversely, the catalytic activity of a CuO/Al$_2$O$_3$ catalyst has been reported to significantly decrease during supercritical water oxidation owing to the leaching of Cu by the supercritical water [20]. Furthermore, the solvent properties of supercritical water are affected by temperature and pressure, and these changes in the solvent properties can impact the deactivation of catalysts. Therefore, elucidating the effects of supercritical water on the catalytic stability of solid acid catalysts is important, but there are, to the best of our knowledge, no reports in the literature of research on this phenomenon.
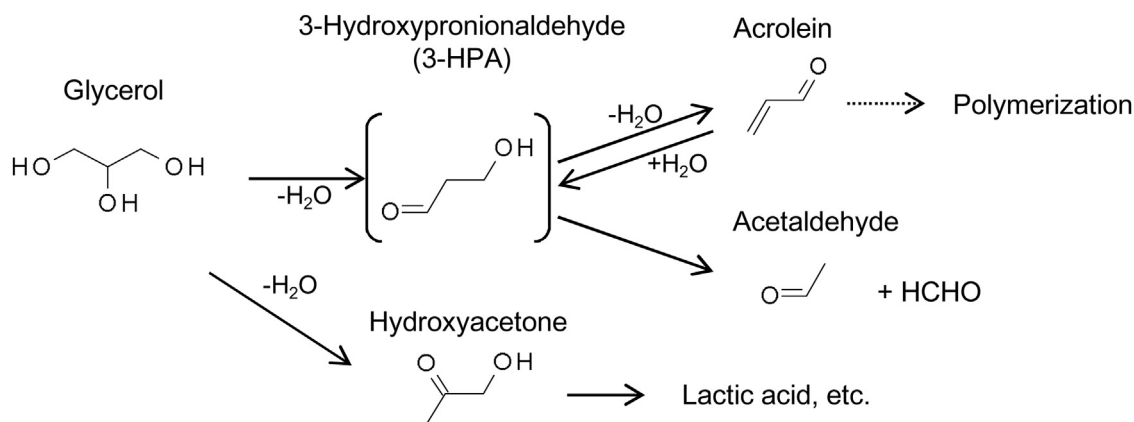
Scheme 1. Main reaction path of glycerol dehydration.
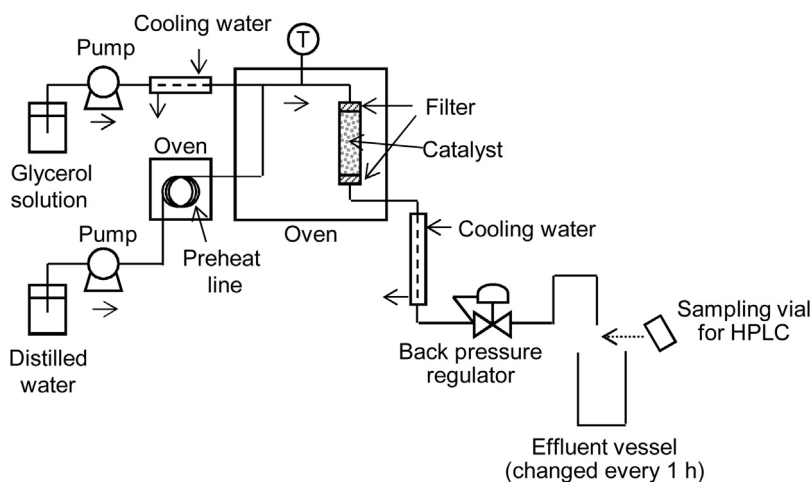

Fig. 1. Schematic diagram of fixed-bed flow reactor.

In this study, the catalytic stability of solid acid catalysts in supercritical water has been investigated using glycerol dehydration as a model reaction. Glycerol dehydration is a typical acid-catalyzed reaction that produces acrolein, which is an important intermediate in the synthesis of acrylic acid, pharmaceuticals, and methionine. Reports of glycerol dehydration using solid acid catalysts have mainly concerned the reaction in the gas phase, and much research on catalyst design has been reported [21,22]. However, the suppression of coking and regeneration of catalysts are also important research topics for solid-acid-catalyzed glycerol dehydration in the gas phase, because coking occurs during the reaction due to the polymerization of acrolein [21–24]. Therefore, we selected this reaction as a model for investigating the effects of supercritical water on coke formation.

In this study, we used WO_X/TiO_2 and NbO_X/TiO_2, which have been reported to show high activity in glycerol dehydration [25,26], as typical solid acid catalysts. The authors have previously conducted kinetic analysis of glycerol dehydration with WO_X/TiO_2 in supercritical water and reported that the catalyst showed high activity under those conditions [27]. The main reaction path for glycerol dehydration based on the previous study is shown in Scheme 1. We investigated coking behavior, catalyst structure change, and active component leaching at different reaction pressures, and the effects of these deactivating processes on catalytic activity are discussed. The purpose of this study was to elucidate how supercritical water and the reaction conditions affect the catalytic stability of solid acids.

2. Material and methods

2.1. Reagents

Glycerol (Kanto Chemical Co., Inc., Japan) and acrolein (Tokyo Chemical Industries Co., Ltd., Japan) were used as purchased. Distilled water was prepared using an RFD240HA distillation unit (Advantec Toyo Kaisha, Ltd., Japan). The aqueous solutions of glycerol and distilled water were degassed by bubbling with N_2 gas prior to use. TiO_2 powder (anatase-type containing 12 wt% rutile-type) and $(NH_4)_{10}W_{12}O_{41}\cdot5H_2O$ were purchased from Wako Pure Chemical Industries, Ltd., Japan, and $C_4H_4NNbO_9\cdot XH_2O$ was purchased from Sigma-Aldrich Japan Co. LLC, Japan.

2.2. Catalyst preparation

WO_X/TiO_2 and NbO_X/TiO_2 catalysts were prepared by an impregnation method. TiO_2 powder was added to an aqueous solution of $(NH_4)_{10}W_{12}O_{41}\cdot5H_2O$ or $C_4H_4NNbO_9\cdot XH_2O$ and stirred for 4 h. After evaporating the water, the obtained powder was dried in a vacuum oven and calcined at 600 °C for 6 h. The WO_X species content was 10 wt% as WO_3 and the NbO_X species content was 10 wt% as Nb_2O_5. The catalysts were in the form of granules of 0.18–0.30 mm in diameter. The 10 wt% WO_X/TiO_2 catalyst and 10 wt% NbO_X/TiO_2 catalyst are hereon abbreviated as WTi and NbTi, respectively.