



Short Communication

Highly durable Pt-supported niobia–silica aerogel catalysts in the aqueous-phase hydrodeoxygenation of 1-propanol

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ABSTRACT

The aqueous-phase hydrodeoxygenation (APHDO) of 1-propanol at 230 °C and 35 bar was studied over 1 wt.% Pt catalysts supported on several metal oxides. Pt catalysts supported on amorphous silica, alumina and niobia aerogels, and crystalline niobic acid calcined at 500 °C showed low activities or deactivation. Under the APHDO condition, these supports experienced a structure transformation to crystalline quartz, boehmite and niobia TT phase. Pt/Nb₂O₅-Al₂O₃ aerogel also suffered from the same crystallization behavior. In contrast, Pt/Nb₂O₅-SiO₂ aerogels with different Nb/(Nb + Si) ratios maintained a good catalytic performance for prolonged reaction periods. Through characterizations of spent catalysts, Nb₂O₅-SiO₂ aerogels were found to retain X-ray amorphous and porous structure. Also, their acid site densities were negligibly changed during the reaction. The catalysts with the Nb/(Nb + Si) ratio of 0.500 and 0.575 reached the molar propane/ethane ratio of about 1.0, indicating that Pt/Nb₂O₅-SiO₂ aerogel catalysts are highly active in the presence of water.

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1. Introduction

An efficient conversion of biomass-derived molecules into fuels and chemicals has been studied in recent years [1–6]. Particularly, much attention has been paid to aqueous-phase processing of C₃ alcohols to produce H₂ and alkanes [7–9]. Huber and coworkers investigated the aqueous-phase hydrodeoxygenation (APHDO) of sorbitol and sugar solutions towards understanding the reaction chemistry [10–12]. In the APHDO process, a series of dehydration and hydrogenation steps takes place over bifunctional catalysts in which an acid is responsible for the dehydration of the reactant and a metal for subsequent hydrogenation. The carbon loss of reactant can be minimized in this case. However, if metal contribution is more dominant than acid, lighter alkanes are produced through dehydrogenation and decarbonylation reactions on metal surfaces. Therefore, the adjustment in the concentration and strength of acid sites is of importance to selectively produce heavier alkanes over bifunctional catalysts. The similar assessment was done on the aqueous-phase reforming and hydrodeoxygenation of C₃ alcohols [7–10,13,14].

In this work, 1-propanol (1-PrOH) was used as a model reactant for oxygenated biomass-derived compounds, due to the difficulty to

dehydrate 1-PrOH with a terminal OH among C₃ alcohols along with the simple product distribution.

Major products in the APHDO of 1-PrOH are CO, CO₂, CH₄, C₂H₆ and C₃H₈ in gas phase. When the dehydration and hydrogenation of 1-propanol occur in sequence (C–O bond cleavage), propane is the main product. In contrast, ethane and CO are formed by the dehydrogenation and decarbonylation (C–C bond cleavage). CO further undergoes the water–gas shift into CO₂ and methanation into CH₄. Therefore, if it is desired to lower the oxygen content in products and minimize carbon loss by suppressing the cleavage of C–C bond, an acid part of bifunctional catalyst responsible for the dehydration of 1-PrOH is then crucial, as in the case of sorbitol [10].

Niobium oxides have been found to be active in acid-catalyzed reactions, even in the presence of water [15–18]. It was reported that amorphous niobium oxide is composed of distorted NbO₆ octahedra and NbO₄ tetrahedra [19,20]; however, it suffers from poor hydrothermal stability, resulting in both a poor activity and low surface area after use [21,22]. This predicts that the texture, structure or acidity of niobia may be changed under aqueous-phase reaction conditions due to high temperature and H₂ pressure in water. The prediction is supported by the recent report of Hensen and coworkers that boehmite formation is observed for spent Pt/γ-Al₂O₃ and Pt/SiO₂-Al₂O₃ catalysts in the aqueous-phase glycerol reforming [7]. Therefore, the catalyst stability is an important issue in the APHDO reaction, besides a superior catalytic performance.

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