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Direct conversion of cellulose into polyols over Ni/W/SiO_2-Al_2O_3

In Gu Baek, Su Jin You, Eun Duck Park *

Division of Energy Systems Research and Department of Chemical Engineering, Ajou University, San 5 Woncheon-dong, Yeongtong-gu, Suwon 443-749, Republic of Korea

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ABSTRACT

The direct conversion of cellulose into polyols over Ni/W/SiO_2-Al_2O_3 catalysts with different Al molar fractions was examined. For comparison, Cu/W/SiO_2-Al_2O_3, Fe/W/SiO_2-Al_2O_3, and Co/W/SiO_2-Al_2O_3 were also evaluated. The bulk crystalline structure was determined using X-ray diffraction (XRD). The surface acidity was probed via temperature-programmed desorption of ammonia (NH_3-TPD). The textural properties were investigated using N_2 physisorption. The metal contents were confirmed via inductively coupled plasma–atomic emission spectroscopy (ICP-AES). Among the various metal catalysts, Ni/W/SiO_2-Al_2O_3 was confirmed to be the most favorable for hydrogenolysis of cellulose into polyols. The effect of the Al molar fraction in SiO_2-Al_2O_3 on this reaction over Ni/W/SiO_2-Al_2O_3 was also investigated. It was found that the polyol yield was closely related to the total acidity of the support. Compared to Ni/W/SBA-15, Ni/W/SiO_2-Al_2O_3 (Al/(Al + Si) = 0.6) showed better stability during the recycling test. The catalyst deactivation was confirmed to be caused by metal leaching.

1. Introduction

The current chemical and energy industries are based on petroleum, coal, and natural gas, which have limited reservoirs and are nonrenewable. Because of increasing concern about shortages of fossil fuels and global warming due to CO_2 accumulation, lots of attention has been paid to the utilization of renewable resources as feedstocks for the chemical and energy industries. Among the proposed renewable resources, biomass has attracted considerable attention because of its abundance and carbon-neutrality.

Lignocellulosic biomass is mainly composed of cellulose, hemicelluloses, and lignin. Among them, cellulose is quite attractive as a starting material, because it is the largest component of the biomass and it is non-edible. However, it is difficult to hydrolyze cellulose and transform it into chemicals and fuels because of its robust crystalline structure with a linkage of β-1,4-glycosidic bonds and hydrogen bonds (Cabiac et al., 2011; Eggeman and Elander, 2005; Mosier et al., 2005; Rinaldi and Schüth, 2009).

So far, there have been several studies on the conversion of lignocellulosic materials into glucose, polyol, 5-HMF, oil, organic acid, and gaseous hydrocarbons using various processes (FitzPatrick et al., 2010; Huber et al., 2006). Polyols, one category of cellulose-derived products, are key intermediates in the manufacture of perfumes, beer, pharmaceuticals, ink, etc. Cellulose has been reported to be transformed into polyols in the presence of hydrogen over various noble metal catalysts, viz. Pt/γ-Al_2O_3 (Fukuoka and Dhepe, 2006), Ru/C (Luo et al., 2007), Ru/CNT (Deng et al., 2009; Wang et al., 2011), Pt/Na(H)-ZSM-5 (You et al., 2011) and Pt/carbon black (Kobayashi et al., 2011). Besides noble metal catalysts, transition metal-based catalysts have also been used. Ni–W_2C/activated carbon (Ji et al., 2008), Ni–W/SBA-15 (Zheng et al., 2010), and Ni–W_xC/CMK-3 (Zhang et al., 2010) were reported to be active for the production of ethylene glycol. Ni_2P/activated carbon was also proposed to be active for sorbitol formation (Ding et al., 2010). To facilitate the hydrolysis of cellulose, some combined catalyst systems have also been proposed: ionic liquid-stabilized Ru nanoparticles (Zhu et al., 2010), heteropolyacids combined with Ru/C (Geboers et al., 2010; Palkovits et al., 2011), mineral acid combined with Ru/C (Liang et al., 2011; Palkovits et al., 2010), and mineral acid combined with Ru/USY (Geboers et al., 2011).

Among the proposed catalyst systems, supported NiW catalysts appear to be promising because they have been reported to be quite effective for polyol synthesis and are rather inexpensive compared with noble metal catalysts. The support is an important ingredient in supported catalysts, because it determines the dispersion of active metal species, chemical stability, and mechanical strength. Furthermore, the support can provide an additional site to provoke other chemical reactions. A solid acid support has been frequently utilized in supported noble metal catalysts to facilitate the hydrogenolysis of cellulose. Therefore, it can be anticipated that the introduction of a solid acid support into supported NiW catalysts would be beneficial for the direct conversion of cellulose into polyols. In this study, we chose SiO_2-Al_2O_3 as a solid acid support, because its acidity can be controlled by changing its Al fractions. In addition, we also examined the effects of promoters (Ni, Cu, Fe, and Co) in supported W catalysts on the catalytic activity for this reaction.

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* Corresponding author. Tel.: +82 31 219 2384; fax: +82 31 219 1612.
E-mail address: edpark@ajou.ac.kr (E.D. Park).

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