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WO_x modified Cu/Al_2O_3 as a high-performance catalyst for the hydrogenolysis of glucose to 1,2-propanediol

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ABSTRACT

Glucose is one of the most important platform molecules of biomass in nature. The selective hydrogenolysis of glucose to 1,2-PDO is still a challenge. However, The hydrogenolysis of fructose has higher activity and selectivity to 1,2-PDO. Therefore, A series of $Cu\text{-}WO_x/Al_2O_3$ catalysts with high activity for glucose isomerization to fructose and fructose hydrogenolysis to 1,2-PDO were designed for glucose hydrogenolysis to 1,2-PDO. The W surface density was controlled as low as 0.8 W/nm^2. The low W surface density could make the WO_x species present as isolated WO_4 structure, which could only provide more Lewis acid sites. As a result, the isolated WO_4 species could form a complex with glucose and then promote the isomerization of glucose to fructose. The isolated WO_4 species also have coverage, dispersion, and electronic effects on copper sites, resulting more stable copper sites and proper amount of hydrogenation sites on $Cu\text{-}WO_x/Al_2O_3$ surface. The correlations between the ratio of Lewis acid amount to Cu surface area and the selectivity of 1,2-PDO suggest that the hydrogenolysis of glucose to 1,2-PDO follows the bifunctional reaction route which contains the reactions on Lewis acid and metal sites. Furthermore, the highest 1,2-PDO selectivity of 55.4% was obtained on $Cu\text{-}WO_x(0.8)/Al_2O_3$.

1. Introduction

Increasing interests have been stimulated in developing novel chemical processes based on renewable biomass materials for producing energy and chemicals in view of the depletion of fossil resources and ongoing climate change [1–4]. Among biomass based feedstocks, glucose, as the monomer of cellulose, is an attractive platform chemical which can be efficiently converted into various chemicals, fuels, foods, medicines [5]. Furthermore, it is the most abundant monosaccharide and readily available from the hydrolysis of cellulose by mineral acids [5]. Therefore, the catalytic transformation of glucose is of great importance for biomass utilization. On this respect, the chemical routes for monosaccharide reactions such as oxidation, dehydration, esterification, hydrogenation, and hydrogenolysis have been reported on many reviews [2,6–9]. Many value-added chemicals and biofuels such as 5-hydroxymethylfufural (HMF), 2,5-dimethylfuran, levulinic acid, γ-valerolactone, gluconic acid, pentanoic acid ester, and various polyols have been studied extensively recently [10]. Especially, hydrogenolysis, which results in the cleavage of C—C and C—O bonds by hydrogen, can produce valuable platform chemicals such as propanediol (PDO) and ethylene glycol (EG) that are already integrated in today's value chain. Furthermore, the hydrogenolysis of glucose in aqueous solution can avoid the fatal disadvantages in biomass conversion, such as the feedstock transportation, batch reaction, coking, organic solution, environment pollution, etc. All these merits make glucose an ideal feedstock in future large-scale biorefining. Therefore, the process of glucose hydrogenolysis in aqueous solution is respected to bear the potential to bridge currently available technologies and the future biomass-based refinery concepts [2].

In the earliest stage of the hydrogenolysis reaction of glucose and its derived-polyols sorbitol, glycerol was considered as the most desirable product. However, with the surplus of glycerol from biodiesel production, the importance of polyols-related value-added chemicals has shifted towards 1,2-propanediol (1,2-PDO) and ethylene glycol (EG). Furthermore, 1,2-PDO is an industrially

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important chemical and is extensively used in the production of polyester resins, pharmaceuticals, tobacco humectants, paints, cosmetics and antifreeze [11]. It is currently produced at an industrial scale using petroleum based propylene as the carbon feedstock. The hydrogenolysis of biomass-derived glucose to 1,2-PDO provides a sustainable and economic route instead of the oxidation of fossil fuel-derived propylene.

Cu, Ni, Ru based catalysts together with base additives such as CaO were often used for the hydrogenolysis of glucose and sorbitol, and a mixture of lower polyols such as glycerol, EG, and 1,2-PDO was mainly obtained. For example, Ye [12] reported a Ce-promoted Ni/Al_2O_3 catalyst for aqueous-phase hydrogenolysis of sorbitol to glycols. At 513 K and 7.0 MPa, above 90% of sorbitol conversion and 55–60% of glycol selectivities were obtained. Chen [13] found that the Ni/MgO catalyst with Ni/MgO ratio of 3:7 exhibited the best performance for sorbitol hydrogenolysis at 473 K and 4 MPa H_2, with 67.8% conversion and 80.8% total selectivity of EG, 1,2-PDO and glycerol. Banu [14] studied the conversion of sorbitol on Ni-NaY and Pt-NaY catalysts. They found that 1,2-PDO was the major product on Ni-NaY and glycerol was the main product on Pt-NaY. Meanwhile, the highest 1,2-PDO selectivity of 72% was achieved at 59% sorbitol conversion on Ni(6%)-Pt(1%)/NaY at 493 K and 6 MPa. A copper-chromium catalyst was more selective for 1,2-PDO. As reported by Zartman [15], a 60% yield of 1,2-PDO was obtained from glucose hydrogenolysis in supercritical ethanol. The CuCr catalyst was also reported to be efficient for the hydrogenolysis of cellulose to 1,2-PDO, with the yield of 42.6% [16]. Apparently, the study still encounters many problems such as poor activities and selectivities, harsh condition, and environmental pollution. Moreover, safe, efficient and economic catalysts are the key factor for the selective conversion of glucose to 1,2-PDO in aqueous solution.

It is well known that the hydrogenolysis of saccharides and polyols can be performed through a bifunctional reaction pathway that involves three primary reactions, C—O bond cleavage on acid sites, C—C bond cleavage and C=O/C=C bond hydrogenation on metal sites [17–19]. Furthermore, retro-aldol condensation is the key C—C bond cleavage reaction and occurs on metal sites [17]. However, it is well known that the retro-aldol condensation of glucose mainly produces C_2 and C_4 polyols, and the conversion of glucose to C_3 polyols includes two steps: the isomerization of glucose to fructose, which can be promoted by Lewis acid; the retro-aldol condensation of fructose to dihydroxyacetone and glyceraldehyde [20,21]. Therefore, based on the understanding of the reaction pathway, an efficient bifunctional catalyst with high activity for glucose isomerization, fructose retro-aldol condensation, dehydration and hydrogenation is required for the selective conversion of glucose to 1,2-PDO. Among the catalysts, Ni and Ru catalysts were frequently used for the hydrogenolysis of sugars and sugar alcohols due to their high activity for C—C bond cleavage. However, excessive C—C bond scission often happened, and large amount of unwanted products such as methane were formed [22]. It is known that copper catalyst has high activity for C—O bond cleavage and low activity for C—C bond cleavage. Such properties of copper based catalysts are suitable for the hydrogenolysis of glucose to glycols [22]. Moreover, the application of cheap metal can improve the economy of the hydrogenolysis route, which is one of the main challenges of the transformation process of renewable feedstocks [2]. As for the acid sites, alumina is a typical industrial support with large amount of acid sites on the surface. Furthermore, many studies have also been performed on the development of acid sites on tungsten oxide supported on alumina catalyst as a function of W surface density [23,24]. The studies turned out that the acid amount and acid species were easily tuned by changing the surface density of W. Furthermore, due to the strong interaction between the oxides, the WO_x phase is molecularly dispersed as a two-dimensional metal oxide overlayer on a high surface area support oxide with a high stability [24]. The ratio of C—C/C—O bond cleavage can be tuned by modulating the concentration of acid to metal sites. A good balance between the two functions is very important to obtain a high yield of target polyols. Therefore, a non-noble Cu-WO_x/Al_2O_3 catalyst with different ratios of acid to metal sites by changing the density of W was designed. Cu/Al_2O_3 with proper activity for C—C/C—O bond cleavage and C=O bond hydrogenation showed a high activity for the hydrogenolysis of fructose to 1,2-PDO, and high dispersed WO_x species have a high selectivity for the isomerization of glucose to fructose. The synergy effect of the catalytic active site promotes glucose conversion and 1,2-PDO selectivity. This work focuses on the effect of W on the properties and catalytic performance of the Cu-WO_x/Al_2O_3 catalysts.

2. Experiment

2.1. Catalyst preparation

Cu/Al_2O_3 and WO_x modified Cu/Al_2O_3 catalysts (denoted as Cu-WO_x/Al_2O_3) with different WO_x weight loadings in the range of 1–7 wt% were prepared by a stepwise impregnation method. Firstly, γ-Al_2O_3 (purchased from Sinopharm Chemical Reagent Co., Ltd, China) was impregnated for 12 h with a certain amount of $(NH_4)_6W_7O_{24}\cdot 6H_2O$ (Sinopharm Chemical Reagent Co., Ltd, China) aqueous solution. The impregnated sample was dried at 120 °C overnight. Afterwards, they were calcined at 600 °C for 4 h. The obtained sample was then impregnated for 12 h with an aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (Sinopharm Chemical Reagent Co., Ltd, China). After impregnation, the sample was dried at 120 °C overnight, followed by calcined at 350 °C for 4 h. The catalysts were labeled as Cu-$WO_x(y)/Al_2O_3$, in which y stands for the surface density of W (atoms/nm^2). The Cu/Al_2O_3 catalyst was prepared using the stepwise impregnation method mentioned above.

2.2. Catalyst characterization

ICP optical emission spectroscopy (Optima2100DV, PerkinEler) was performed to determine the chemical compositions of calcined catalysts.

BET surface areas were measured on a micromeritics ASAP 2420 instrument. All the samples were degassed at 110 °C for 1 h and 350 °C for 8 h prior to the measurement.

The surface areas of copper were calculated using N_2O chemisorption method performed based on the assuming spherical shape of the copper metal particles and 1.4×10^{19} copper atoms/m^2 [25,26]. Before the measurements, 200 mg sample was reduced by flowing H_2 at 250 °C for 2 h, followed by purging with He for 1 h. After cooled down to 50 °C, the sample was flushed with 10 vol.% N_2O/N_2 (50 mL/min) flow for 30 min. Then changed the gas flow to Ar (50 mL/min) and held for 30 min to clean the catalyst surface, finally the H_2-TPR was recorded with the 10 vol% H_2/Ar flow.

Powder X ray diffraction (XRD) patterns were recorded on a D2/max-RA X-ray diffractometer (Bruker, Germany), with Cu-Kα radiation operated at 30 KV and 10 mA. The 2θ angle was scanned in the rage of 10–80°.

H_2-TPR experiments were carried out on the Auto Chem II 2920 equipment (Micromeritics, USA) with a TCD detector. The sample (200 mg) was loaded in a quartz reactor and flushed with a 10 vol.% H_2/Ar flow at 50 °C. Then an isopropyl alcohol gel (−88 °C) cooled trap was added to condense the water vapor. The hydrogen consumption was monitored from 50 °C to 600 °C using a heating rate of 10 °C/min.

Raman spectra were recorded on a LabRAM HR800 System equipped with a CCD detector at room temperature. The 532 nm of the air-cooled frequency-doubled Nd-Yag laser was employed as the exciting source with a power of 30 MW.