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ARTICLE

Reforming and Hydrogenolysis of Glycerol over Ni/ZnO Catalysts Prepared by Different Methods

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Abstract: The catalytic conversion of glycerol to 1,2-propanediol (1,2-PDO) is generally conducted batch-wise in an autoclave in the presence of high pressure H_2. The reforming and hydrogenolysis of glycerol to 1,2-PDO over Ni/ZnO catalysts in a continuous flow fixed-bed reactor without added H_2 was reported. The Ni/ZnO catalysts were prepared by wetness impregnation (WI), co-precipitation (CP), hydrothermal treatment (HT), and carbon microsphere hard-templating (CT) methods. The catalysts were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), transmission electron microscopy (TEM), and H_2 titration. At a low weight hourly space velocity (WHSV) of glycerol, the 1,2-PDO produced got degraded to ethanol and gas phase products over catalysts with high Ni dispersion, while at a high WHSV, the selectivity for 1,2-PDO was limited by the hydrogenation of the acetol intermediate. At the optimized WHSV, the catalyst with a higher Ni dispersion was more selective for 1,2-PDO, and over the Ni/ZnO catalyst with the highest Ni dispersion, the highest selectivity of 54.9% for 1,2-PDO was obtained at a glycerol conversion of 85.4% at the WHSV of 0.84 h^{-1}.

Key words: nickel; zinc oxide; glycerol; reforming; hydrogenolysis; 1,2-propanediol; dispersion degree

Due to the non-sustainability of fossil fuels, researchers have turned to renewable resources [1,2], of which the production of biodiesel from oil and fats by transesterification with alcohol is representative [3,4]. Generally, the production of ten tons of biodiesel will yield one ton of glycerol as byproduct [5]. Thus, the transformation of glycerol to valuable commodity chemicals has attracted considerable attention. For example, researchers have developed various heterogeneous catalytic routes such as dehydration to acrolein [6], partial oxidation to dihydroxypropanone [7,8], aqueous-phase reforming (APR) to H_2 [9–11], and hydrogenolysis to 1,2-propanediol (1,2-PDO)/1,3-propanediol (1,3-PDO) [12–15]. 1,2-PDO is a chemical with wide applications in daily life, pharmaceutical, and chemical synthesis processes. Currently, 1,2-PDO is mainly produced by the petrochemical route through the hydration of propylene oxide [1]. It is evident that the transformation of biomass-derived glycerol to 1,2-PDO is more sustainable.

The hydrogenolysis of glycerol to 1,2-PDO is mainly catalyzed by Cu or Ru-based catalysts. Yuan et al. [13] reported that the conversion of glycerol and the selectivity for 1,2-PDO both exceeded 90% over a $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$-CP catalyst with the aid of NaOH. Ru-based catalysts exhibit higher activity than Cu-based catalysts, but since Ru tends to break the C–C bond, they lead to lower 1,2-PDO selectivity. Feng et al. [14] found that as compared to Ru on other supports, Ru supported on TiO_2 showed the highest activity, but the selectivity for 1,2-PDO was only about 50%. By mixing LiOH with Ru/TiO_2, the conversion of glycerol and selectivity for 1,2-PDO reached 89.6% and 86.8%, respectively [15].

In the literature, the hydrogenolysis of glycerol to 1,2-PDO is usually conducted under a relatively high H_2 pressure (5–8 MPa) [16,17], which imposes high demands on reactor materials and operation safety. Also, using H_2 increases the production cost. D'Hondlt et al. [18] first reported that glycerol hydrogenolysis to 1,2-PDO can be achieved without added H_2 through a combined APR-hydrogenolysis strategy. Over a catalyst with reforming ability, H_2 generated in the APR proc-

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ess (Reaction 1 in Scheme 1) serves as an in situ hydrogen source for the subsequent hydrogenolysis reactions (Reactions 2 and 3 in Scheme 1). Ideally, seven H_2 molecules are generated by the APR of one glycerol molecule [9], and these H_2 molecules hydrogenolyze seven glycerol molecules to seven 1,2-PDO molecules. The highest theoretical selectivity for 1,2-PDO is 87.5% in this reaction scheme [18]. This strategy has been validated in several published papers [19–22]. For example, Roy et al. [20] obtained glycerol conversion of 50.1% and 1,2-PDO selectivity of 47.2% over physically mixed Pt/Al_2O_3 and Ru/Al_2O_3 (mass ratio of 1:1) catalysts under a N_2 atmosphere. Gandarias et al. [21] reported a 1,2-PDO selectivity of 35.3% at a glycerol conversion of 26.6% over Si-Al mixed oxides-supported Pt catalyst under a N_2 atmosphere.

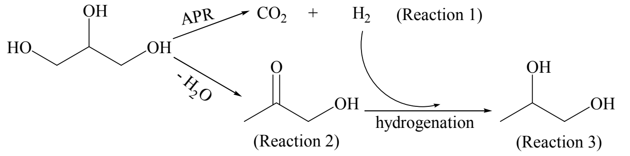
The advantages of APR-hydrogenolysis of glycerol to 1,2-PDO include (1) no need for external H_2, thus improving reactor safety, and (2) the system pressure is low, thus cutting down on reactor cost and improving operational safety [20]. However, almost all catalysts reported so far for APR-hydrogenolysis of glycerol to 1,2-PDO are precious metals, and there is much room for the improvement of the selectivity to 1,2-PDO [20–22]. Non-precious metal Ni has both APR and hydrogenolysis activities, but Ni-based catalysts have rarely been explored [19]. In this work, we prepared Ni/ZnO catalysts by different methods and used them for the APR-hydrogenolysis of glycerol to 1,2-PDO. Our results showed that these catalysts can convert glycerol to 1,2-PDO effectively in the absence of added H_2. The effect of the preparation method on the selectivity for 1,2-PDO is discussed.

1 Experimental

1.1 Catalyst preparation

The Ni/ZnO catalysts were prepared by wetness impregnation (WI), co-precipitation (CP), hydrothermal treatment (HT), and carbon microsphere-templating (CT) methods.

WI method. First, 1.556 g of $Ni(NO_3)_2\cdot6H_2O$ was dissolved in 10 ml of deionized water at room temperature. Then, 1.790 g of ZnO was added into the solution. The preparation process of ZnO was similar to the CP method described below but without a nickel salt. After it was homogeneously mixed, the mixture was dried in a water bath at 333 K. The solids were dried at 373 K overnight and calcined at 773 K for 4 h with heating at a heating rate of 2 K/min. This sample was denoted as NiO/ZnO-WI. After reduction, the catalyst was denoted as Ni/ZnO-WI.



Scheme 1. Reaction pathway of glycerol reforming and hydrogenolysis to 1,2-propanediol (1,2-PDO).

CP method. The preparation was based on the method described by Ryzhikov et al. [23]. First, 1.556 g of $Ni(NO_3)_2\cdot6H_2O$ and 6.576 g of $Zn(NO_3)_2\cdot6H_2O$ were dissolved in 137.5 ml of deionized water at room temperature. The mixed solution was maintained in a water bath at 333 K under vigorous stirring. Then, 60 ml of 0.5 mol/L Na_2CO_3 solution (ca. 10% alkali excess) was added into the mixed solution by a peristaltic pump at a speed of 2 ml/min. The resulting suspension was aged in the water bath for another 4 h under vigorous stirring. The precipitate was washed by deionized water six times to remove residual base and Na^+ ions, using 300 ml of deionized water for each washing. Finally, the precipitate was dried at 373 K overnight and calcined at 773 K for 4 h with a heating rate of 2 K/min. This sample was denoted as NiO/ZnO-CP, and the reduced catalyst was denoted as Ni/ZnO-CP.

HT method. The precipitation and aging processes were the same as in the CP method. The aged precipitate was transferred into a 250 ml autoclave for a hydrothermal treatment at 373 K for 24 h. The subsequent washing and calcination processes were also the same as the CP method. This sample was denoted as NiO/ZnO-HT, and the reduced catalyst was denoted as Ni/ZnO-HT.

CT method. Carbon microspheres were prepared using the method in Ref. [24]. First, 0.5 g carbon microspheres were added into a $Ni(NO_3)_2$ and $Zn(NO_3)_2$ mixed solution obtained as described in the CP method. The mixture was vigorously stirred for 1 h. The successive preparation steps were the same as in the HT method. This sample was denoted as NiO/ZnO-CT, and the reduced catalyst was denoted as Ni/ZnO-CT.

1.2 Catalyst characterization

The bulk composition was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, IRIS Intrepid). The Brunauer-Emmett-Teller (BET) surface area ($A_{\rm BET}$) and porosity were measured by N_2 adsorption at 77 K on a Micromeritics TriStar3000 apparatus. Prior to the measurement, the samples were degassed at 473 K for 2 h under flowing N_2 atmosphere. Room temperature H_2 titration was conducted to determine Ni surface area ($A_{\rm act.}$). The amount of chemisorbed H_2 was monitored by a thermal conductivity detector (TCD). H/Ni stoichiometry of 1 and a surface atom density of 1.54×10^{19} Ni atom/m^2 were assumed. The average Ni particle size was estimated using the hemisphere model. Thermogravimetric analysis (TG, TGA7) at a heating rate of 10 K/min was employed to investigate the thermal decomposition behavior of the precursor of NiO/ZnO-CT in air. Powder X-ray diffraction (XRD) was conducted on a Bruker AXS D8 Advance X-ray diffractometer using Cu K_α radiation (λ = 0.15418