



Hydrogenolysis of glycerol on bimetallic Pd-Cu/solid-base catalysts prepared via layered double hydroxides precursors

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ABSTRACT

A series of bimetallic Pd-Cu/solid-base catalysts were prepared via thermal decomposition of $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ layered double hydroxides precursors and used in hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO). X-ray diffraction (XRD), scanning electron microscopy (SEM) and N_2O oxidation and followed H_2 titration characterizations confirmed that well structured layered double hydroxides $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ crystals could be prepared when the amount of added Pd was less than $x < 0.04$. Pd and Cu dispersed highly in reduced $\text{Pd}_x\text{Cu}_{0.4}/\text{Mg}_{5.6-x}\text{Al}_2\text{O}_{8.6-x}$ and Pd improved the reduction of Cu. Hydrogenolysis of glycerol proceeded easily on bimetallic Pd-Cu/solid-base catalysts than separated Pd and Cu. On $\text{Pd}_{0.04}\text{Cu}_{0.4}/\text{Mg}_{5.56}\text{Al}_2\text{O}_{8.56}$, the conversion of glycerol and selectivity of 1,2-PDO reached 88.0 and 99.6%, respectively, at 2.0 MPa H_2 , 180 °C, 10 h in ethanol solution. And this catalyst is stable in five recycles. It was concluded that H_2 -spillover from Pd to Cu increased the activity of $\text{Pd}_x\text{Cu}_{0.4}/\text{Mg}_{5.6-x}\text{Al}_2\text{O}_{8.6-x}$ in hydrogenolysis of glycerol.

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1. Introduction

Recently, there is an increasing interesting on using biodiesel as an alternative fuel [1,2]. The rapid rising production of biodiesel has led to a drastic surplus of glycerol [2]. Many biodiesel production factories now view crude glycerol as a waste. Many efforts have been reported on the conversion of glycerol into value-added products, such as catalytic oxidation of glycerol to glyceric acid [3–6] and dihydroxyacetone [4–6], dehydration of glycerol to acrolein [7–10] and hydrogenolysis of glycerol to propanediols [11–16]. Among these reported technologies, catalytic synthesis of propanediols from glycerol instead of the expensive hydration of petro-based propylene oxide is more favorable in green chemistry and industrial application [2,11–24].

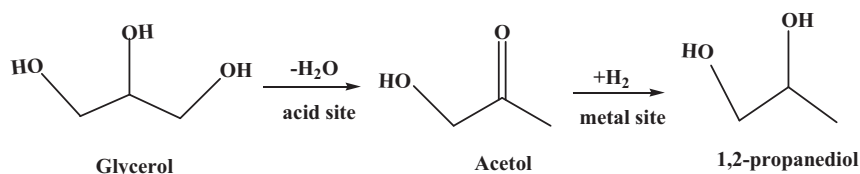
In published papers, hybrid Rh/C + H_2WO_4 [12], Ru/C (or Rh/SiO₂) + Amberlyst [13,14], Pt/SiO₂–Al₂O₃ [11] and ruthenium-doped acidic heteropoly salt $\text{Cs}_{2.5}\text{H}_{0.5}[\text{PW}_{12}\text{O}_{40}]$ were studied in detail in hydrogenolysis of glycerol to propanediols. It was suggested that glycerol hydrogenolysis performed in consecutive glycerol dehydration to acetol (on acid sites) and acetol hydrogenation to propanediols (on metal particles) in acidic conditions (see Scheme 1) [25–43]. But the conversion of glycerol was low and mainly noble metals were reported in acidic conditions. On the other hand, it was reported that NaOH can accelerate the conver-

sion of glycerol in combined Pt/C + NaOH [31,32], Ru/TiO₂ + NaOH [44] and Cu/ZnO + NaOH [45] catalytic solutions. It was deduced that glycerol hydrogenolysis proceeded in a distinct dehydrogenation–dehydration–hydrogenation mechanism in base solutions (see Scheme 2) [31–42]. But NaOH also catalyzed the cleavage of C–C bond and increased the formation of undesired products like ethylene glycol, ethanol and methanol [31,32]. And the addition of NaOH inevitably resulted in other drawbacks such as the reaction mixture needs further neutralization and environmental pollution.

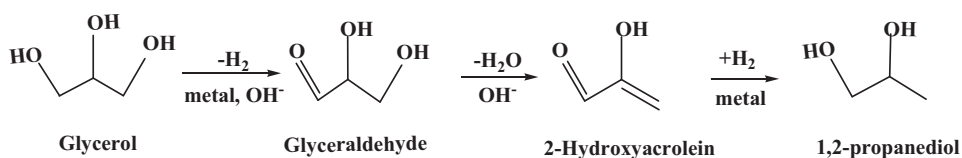
According to these mechanisms, we thought that a solid bifunctional catalyst consisting of both metal and acid/base sites should be capable for this reaction. Choosing solid-base and/or solid-acid as a co-catalyst and support would be a good substitute for the reported hybrid catalysts. Because crude glycerol derived from biodiesel production contains a variety of impurities (such as unreacted catalysts, NaOH or other alkali metal hydroxides) and these contaminants are poisons to solid-acid [33–35], solid-base should be a good co-catalyst and support in industrial application.

In our previous works, hydrotalcite, MgO, Al₂O₃, HZSM-5 and H-Beta supported Pt catalysts were first tested in hydrogenolysis of glycerol. It was found that solid-base (such as hydrotalcite and MgO) supported Pt catalysts exhibited predominant activity and higher 1,2-propanediol (1,2-PDO) selectivity than that of solid acids (Al₂O₃, H-ZSM-5 and H-Beta) [36]. And MgO supported copper is also active in this reaction [37]. More recently, we found that a homogeneously dispersed copper on layered solid-base catalyst is more effective in the hydrogenolysis of glycerol in aqueous solution. The best yield of 1,2-PDO reached 78.5% at 180 °C, 3.0 MPa

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Scheme 1. Glycerol hydrogenolysis in acidic conditions.



Scheme 2. Glycerol hydrogenolysis in base solutions.

H_2 and 20 h [38]. In these works, it was disclosed that the activity of bi-functional Cu/solid-base catalysts increased with the alkali strength of solid-base. However, the influence of active metals (hydrogenation center in Scheme 2) in bi-functional metal/solid-base catalysts has not been specified.

In this work, a series of bimetallic Pd-Cu/solid-base catalysts were prepared via thermal decomposition of $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ layered double hydroxides precursors. And these catalysts were used in hydrogenolysis of glycerol to 1,2-PDO in different solvents at low hydrogen pressure (2.0 MPa) and short time (10 h). These catalysts were characterized by N_2 -adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature-programmed reduction with H_2 (H_2 -TPR) and N_2O oxidation and followed H_2 titration. The structure-property relationships of these bimetallic Pd-Cu/solid-base catalysts in hydrogenolysis of glycerol to 1,2-PDO were discussed.

2. Experimental

2.1. Catalyst preparation

A series of Pd-containing $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ layered double hydroxides precursors were first prepared by coprecipitation. Calculated amount of PdCl_2 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, Shanghai Chemicals, China) were dissolved together in 400 mL deionized water, which was referred as solution A. Solution B was the mixture of Na_2CO_3 and NaOH (AR, Shanghai Chemicals, China) with concentration of 0.25 and 0.8 mol/L, respectively. Solutions A and B were simultaneously added into a glass reactor under vigorous stirring at room temperature and a pH value of 9.5. The slurry was aged at 120°C for 20 h, filtered off, and washed thoroughly with distilled water until free of Cl^- . The precipitate was then dried at 80°C overnight and identified as $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$, in which x referred to amount of added Pd. The layered double structure of prepared $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ sample was confirmed by XRD (see Fig. 1).

Secondly, these Pd-containing layered double hydroxides were calcined at 400°C in a stationary air for 4 h and the product catalysts were identified as $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2\text{O}_9$ and used for characterization. After hydrogen reduction at 300°C for 1 h, these catalysts were identified as $\text{Pd}_x\text{Cu}_{0.4}/\text{Mg}_{5.6-x}\text{Al}_2\text{O}_{8.6-x}$, in which x referred to amount of added Pd.

2.2. Characterizations

Actual composition of the prepared $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ precursors was checked and confirmed by

inductively coupled plasma-atomic emission spectroscopy (ICP, plasma-Spec-II spectrometer). Samples were first dissolved with aqua regia, and the mixtures were further oxidized with 30% hydrogen peroxide in order to make Pd dissolved completely. N_2 adsorption was measured at its normal boiling point using an ASAP 2010 analyzer (Micromeritics) after pretreated at 250°C for 4 h in vacuum. BET surface area and BJH pore size distribution were calculated using their desorption isotherms. XRD patterns were detected at room temperature on a Rigaku D/WAX-2500 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a 2θ step of 0.02° . SEM images of these hydrotalcite-like samples were taken on a microscope (Leo Series VP 1430, Germany) having silicon detector equipped with energy-dispersive X-ray (EDX) facility (Oxford instruments). Samples were coated with gold using sputter coating to avoid charging. Analysis was carried out at an accelerating voltage of 15 kV. H_2 -TPR studies were carried out in a quartz reactor. Samples were first pretreated at 450°C for 1 h under N_2 at a flow rate of 30 mL/min and cooled to room temperature. A reduction agent (10% H_2/N_2 mixture, 30 mL/min) was shifted and the reactor was heated to 450°C at a ramp of $10^\circ\text{C}/\text{min}$. Effluent gas was dried by powder KOH and the consumption of hydrogen

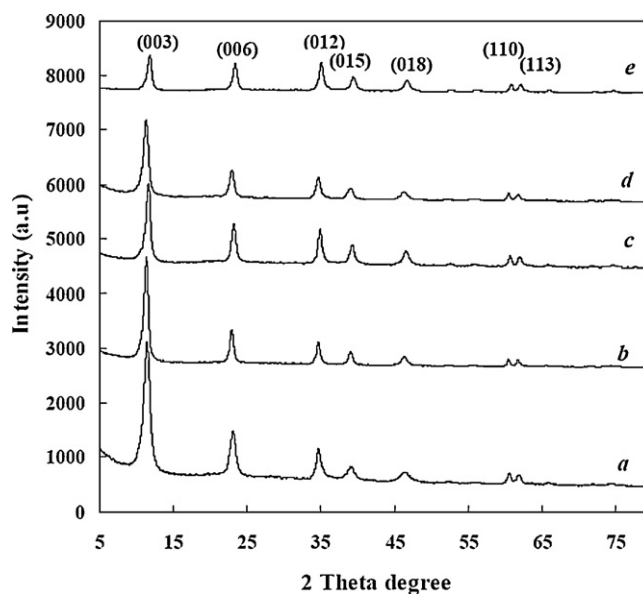


Fig. 1. XRD patterns of fresh $\text{Pd}_x\text{Cu}_{0.4}\text{Mg}_{5.6-x}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ LDHs. (a) $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$; (b) $\text{Pd}_{0.008}\text{Cu}_{0.4}\text{Mg}_{5.592}\text{Al}_2(\text{OH})_{16}\text{CO}_3$; (c) $\text{Pd}_{0.024}\text{Cu}_{0.4}\text{Mg}_{5.576}\text{Al}_2(\text{OH})_{16}\text{CO}_3$; (d) $\text{Pd}_{0.04}\text{Cu}_{0.4}\text{Mg}_{5.56}\text{Al}_2(\text{OH})_{16}\text{CO}_3$; (e) $\text{Pd}_{0.08}\text{Cu}_{0.4}\text{Mg}_{5.52}\text{Al}_2(\text{OH})_{16}\text{CO}_3$.

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