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Hydrogenolysis of glycerol to 1,2-propanediol on copper core-porous silica shell-nanoparticles

Kuo-Tseng Li*, Chih-Hao Wang, Hsien-Chang Wang

Department of Chemical Engineering, Tunghai University, Taichung 40704, Taiwan, ROC

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ABSTRACT

Glycerol hydrogenolysis to 1,2-propanediol (PDO) was investigated in methanol over copper core-porous silica shell-nanoparticles with a Cu/Si atomic ratio range of 1/8–2. These catalysts were prepared by coating silica onto the surface of chemically reduced Cu-polyvinylpyrrolidone colloids, and were characterized with TEM, nitrogen adsorption, XRD, H_2-TPR and NH_3-TPD. In the absence of externally added hydrogen, the catalyst with a Cu/Si atomic ratio of 1 exhibited the best PDO yield (72.8% at 200 °C), which was ascribed to its largest surface area. The intermediate-acetol-yield increased with increasing Cu/Si atomic ratio and reaction temperature. In the presence of externally added hydrogen, the catalyst with a Cu/Si atomic ratio of 2 had the best PDO yield (96.5% at 200 °C), which was ascribed to its greatest copper content and large pore size. The rate of glycerol disappearance exhibited first-order dependence on glycerol concentration. Under identical reaction conditions, Cu@SiO_2 core-shell-catalysts with Cu/Si atomic ratios of 1 and 2 exhibited better performances than a commercial copper chromite catalyst.

1. Introduction

Glycerol is the co-product of biodiesel production industry and its quantity increases rapidly due to the increasing use of biodiesel. Glycerol has become one of the top 12 building blocks of biorefinery because the cost of purified glycerol decreases rapidly [1,2]. The conversion of glycerol into other valuable chemicals is a promising way for solving the oversupply problem of glycerol [3,4].

The hydrogenolysis of glycerol to 1,2-propanediol (shown in Eq. (1)) is one of the possibilities of glycerol utilization [5,6]. 1,2-propanediol is mainly used as a raw material for producing unsaturated polyester resins, antifreeze fluid, solvent, preservative in food and in tobacco products [7].

$$C_3H_5(OH)_3 + H_2 \rightarrow CH_3CH(OH)CH_2(OH) + H_2O \quad (1)$$

Copper-based catalysts, including copper chromite [8–12], Cu–ZnO [13–18], Cu/SiO_2 [19–21], Cu–Al_2O_3 [22–25] and Cu/ZnO /Al_2O_3 [26], are mostly often used for glycerol hydrogenolysis to produce 1,2-propanediol in the presence of high pressure hydrogen. In the literature, Cu/SiO_2 catalysts for glycerol hydrogenolysis were prepared by several different methods, including precipitation-gel [19], homogeneous-precipitation, heterogeneous deposition-precipitation [20], incipient wetness and ion-exchange [21]. Copper-based catalysts exhibit high 1,2-propanediol selectivity, however, the use of high pressure hydrogen gas limits their industrial usage [27,28]. Recently, a Cu–Al oxide catalyst, prepared by a co-precipitation method, was used to catalyze the simultaneous glycerol dehydration and *in situ* hydrogenolysis without externally added hydrogen [29]. The maximum 1,2-propanediol yield obtained with the Cu–Al oxide catalyst was around 50% (75% 1,2-propanediol selectivity at a glycerol conversion of around 70%).

For supported metal catalysts, applicable metal atom mobility appears at about $T_m/3$ (called Hutting temperature) [30]. The melting point of copper is 1357.77 K, therefore, copper atom mobility appears at 453 K. Core-shell structure can be used to prevent the metal sintering of catalysts. Recently, we prepared palladium core-porous silica shell particles (Pd@SiO_2) for catalyzing the hydrogenation of 4-caroxybenzaldehyde [31]. The palladium nanoparticels encapsulated in porous silica shell have been proved to be highly stable for CO oxidation [32].

In this work, hydrogenolysis of glycerol to 1,2-propanediol was studied over copper core-porous silica shell-nanoparticles (denoted as Cu@SiO_2) with several different Cu/Si atomic ratios. The Cu@SiO_2 catalyst was capable of achieving 72.8% 1,2-propanediol yield in the absence of externally added hydrogen.

2. Experimental

2.1. Catalyst preparation and characterization

Cu@SiO_2 core-shell-particles were prepared by coating silica onto the surface of Cu-polyvinylpyrrolidone (PVP) colloids, according

* Corresponding author. Tel.: +886 4 23590262; fax: +886 4 23590009.
E-mail address: ktli@thu.edu.tw (K.-T. Li).

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to the well-known Stober method, which included hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in ethanol, using ammonia as catalyst to initiate the reaction. The Cu-PVP colloids were synthesized by chemical reduction of Cu^{2+} in an alkaline environment using formaldehyde as reducing agent and polyvinylpyrrolidone (PVP) as protecting agent.

The main steps for catalyst preparation were as follows [31]:

1 Prepare an aqueous solution of $Cu(NO_3)_2$ and PVP, containing 5.5 g $Cu(NO_3)_2$ (Strem Chemicals, Newburyport, MA), 25 ml de-ionized water and 19.1 g PVP (molecular weight = 8000; ACROS, Geel, Belgium).
2 Add 7.8 g formaldehyde (Scharlan Chimie, Barcelona, Spain) and 1.4 g NaOH (Showa Chemicals, Tokyo, Japan) to the above solution to synthesize Cu-PVP colloids.
3 Wash the Cu-PVP colloids with acetone (Echo Chemical, Taiwan) for three times and dry the Cu-PVP particles at 100 °C for 12 h.
4 Prepare and sonicate an aqueous (75 ml de-ionized water) solution containing Cu-PVP colloids, ethanol (Echo Chemical, 200 ml), and ammonia in water (25.5 ml).
5 Add TEOS (ACROS; TEOS amount depends on Cu/Si atomic ratio) and agitate the resulting solution at room temperature for 24 h.
6 Collect the $Cu@SiO_2$ core-shell-particles by washing, centrifuging, and drying at 100 °C for 12 h.
7 Calcine the sample at 400 °C for 3 h.
8 Reduce particle in a gas of 5% hydrogen in 95% argon at a heating rate of 1 °C/min to 230 °C, and maintain at 230 °C for 4 h.

The specific surface area and pore size distribution of the catalysts were determined by nitrogen adsorption with a Micromeritics surface area analyzer and porosimetry system (model ASAP 2020). Transmission electron microscopy (TEM) observations were made using JEOL JEM2100F. Crystalline structure was examined by X-ray diffraction (XRD) crystallography on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation. Catalyst acidic properties were measured by temperature programmed desorption of ammonia (NH_3-TPD). Before TPD, the sample was pre-treated in helium at 773 K for 0.5 h. Then the sample was cooled down and was saturated with ammonia at 393 K for 0.5 h. Following catalyst equilibrium in a helium flow at room temperature, NH_3 was desorbed using a linear heating rate of 10 K/min up to 923 K. The catalyst reducibility was studied with a temperature-programmed reduction (TPR) method. TPR was conducted in a quartz tubular reactor filled with 0.15 g catalyst, using 10% H_2 in argon at a flow rate of 60 ml/min and a heating rate of 10 °C/min. The consumption of H_2 was measured using a thermal conductivity detector after removing of water formed with a molecular sieve.

2.2. Reaction studies

Hydrogenolysis of glycerol was carried out with a 600 ml stirred reactor made of stainless steel (supplied by Parr Instruments Co.) with and without externally added hydrogen. In a typical run, a specific amount of glycerol (Alfa Aesar, Ward Hill, MA, USA), 1 g of $Cu@SiO_2$ core-shell-particles prepared above, and methanol (total reaction solution = 50 g) were mixed together and charged into the reactor. The agitator speed was set at 600 rpm, and the reaction mixture was then heated to the desired temperature. For comparison, a hydrogen reduced copper chromite powder (Strem Chemicals, Newburyport, MA) was also used for glycerol hydrogenolysis. At the end of the reaction, the component compositions were determined with a Shimadzu (Kyoto, Japan) high performance liquid chromatography (model: LC-10A) equipped with a 250 mm long C-18 column and a UV detector (wavelength was set at 254 nm). Acetol concentration was measured separately with a Shimadzu gas chromatography (model GC-2014) equipped with a FFAP capillary column. The glycerol conversion was defined as (moles of glycerol reacted)/(moles of glycerol fed to the reactor) × 100%, product yield was defined as (moles of product obtained)/(moles of glycerol fed to the reactor) × 100%.

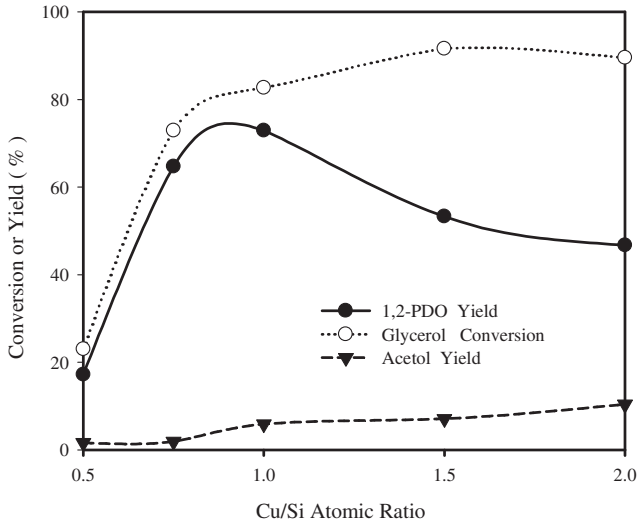

Fig. 1. Variation of glycerol conversion, 1,2-propanediol and acetol yield as a function of Cu/Si atomic ratio (without externally added hydrogen). Reaction conditions: 1 g catalyst in 50 g reaction solution (10 wt.% glycerol in methanol), T = 200 °C, reaction time = 10 h.

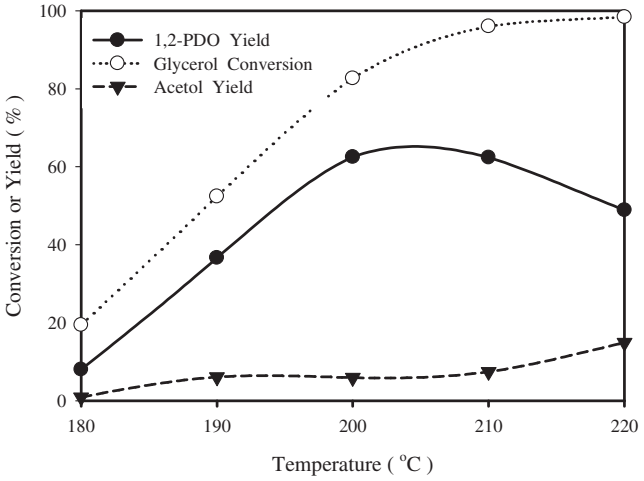

Fig. 2. Influence of reaction temperature on glycerol conversion, 1,2-PDO and acetol yield for the catalyst with a Cu/Si atomic ratio of 1 (without externally added hydrogen). Reaction conditions: 1 g catalyst, 10 wt.% glycerol in methanol, reaction time = 8 h.

3. Results and discussion

3.1. Hydrogenolysis of glycerol in the absence of externally added hydrogen

Fig. 1 presents glycerol conversion, 1,2-propanediol and acetol yields as a function of Cu/Si atomic ratio in the absence of externally added hydrogen. The data were obtained with 10 wt.% glycerol (in methanol) at 200 °C and 10 h using 1 g catalyst. Without externally added hydrogen, the major sources for hydrogenation generation is due to the decomposition of methanol (solvent) on copper surface to produce hydrogen ($CH_3OH = CO + 2H_2$), the amount of methanol decomposition was about 10% at 200 °C. Silica supported copper catalysts have been studied for catalyzing methanol decomposition to produce hydrogen [33].

In Fig. 1, 1,2-PDO yield curve exhibits a volcano shape with a maximum 1,2-propanediol yield of 72.9% at a Cu/Si atomic ratio of 1.