Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Efficient catalytic hydrogenolysis of glycerol using formic acid as hydrogen source

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ARTICLE INFO

ABSTRACT

We describe a sustainable, cost-effective, and highly efficient H_2-free protocol for catalytic hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) using formic acid (FA) as the H_2 source. The process is catalyzed by an earth-abundant and robust Cu-based metal oxide catalyst, in which the high performance of the Cu catalyst for the in situ generation of H_2 gas in the system by highly selective decomposition of FA in an aqueous medium is essential. The activity test results showed that a synergy effect of well-dispersed Cu and amphoteric ZrO_2 is essential for FA decomposition as well as for glycerol conversion to 1,2-PDO. The Cu content of the Cu/ZrO_2 catalyst prepared by the oxalate gel method has a significant role in the FA-mediated glycerol conversion to 1,2-PDO, and a Cu content of 20 wt% on ZrO_2 was identified as the optimum Cu content. Moreover, the creation and maintenance of high component dispersion is essential for high glycerol hydrogenolysis activity of the Cu/ZrO_2 system. Because selective hydrogenolysis with minimum use of external fossil-fuel H_2 is a critical issue in the realization of biorefinery concepts, the procedure described here is expected to be of broad applicability in biomass use.

1. Introduction

Diminishing petroleum reserves and growing concerns about global climate change necessitate the development of fuel and chemical production pathways based on renewable resources such as biomass materials [1,2]. In this respect, glycerol, obtained as a high-volume by-product in the biodiesel process, has emerged as a promising abundant feedstock for the renewable chemicals industry [3–5]. Among various transformations already reported for glycerol, hydrogenolysis to propanediols (PDOs) is of particular interest because of the large numbers of applications of 1,2- and 1,3-PDO (Scheme 1). 1,2-PDO is a major commodity chemical that is currently obtained through the selective hydrolysis of propylene oxide [6–8]. 1,3-PDO has traditionally been considered a specialty

chemical [9,10]; however, it is fast emerging as a significant building block for the manufacture of polyesters such as poly(trimethylene terephthalate). Glycerol hydrogenolysis has mainly been performed using molecular hydrogen (H_2) [4,11–14]. However, high H_2 pressures are generally required to reach acceptable conversion and selectivity. As well as this practical inconvenience, the use of H_2 has some other important drawbacks. First, most of the currently available H_2 gas is still produced from fossil fuels, which makes the process dependent on fossil carbon. In addition, it ignites easily and has high diffusivity, and therefore presents considerable hazards when working at high pressures.

One interesting alternative that could minimize external fossil-fuel H_2 consumption is the use of formic acid (FA), one of the major products formed during biomass processing, as the
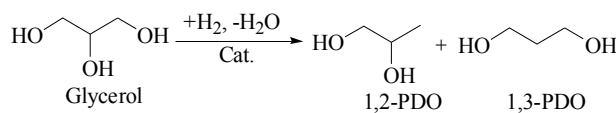
Scheme 1. Reaction for conversion of glycerol to PDOs.

H_2 source. FA has recently attracted considerable interest in the area of green and sustainable chemistry because of its potential as a H_2 carrier and as a means of using CO_2 [3,15]. FA is liquid at room temperature, so it has the added technical advantage that its use as a replacement for H_2 would not be limited by storage and delivery problems [15,16]. Compared with the impressive progress being made in glycerol hydrogenolysis with H_2, very few reports dealing with the direct hydrogenolysis of glycerol using FA as a H_2 source are available. In related previous studies, bimetallic Ni-Cu supported on Al_2O_3 was used as an efficient catalyst for direct hydrogenolysis of glycerol with FA [17]. However, this catalyst has a low inherent efficiency, and the system requires the use of a heavily loaded catalyst and prolonged reaction times at high temperatures (up to 24 h at 220 °C) to improve the hydrogenolysis kinetics. From both practical and economic points of view, a more efficient catalytic transformation that can be carried out at lower reaction temperatures using stoichiometric amounts of FA and glycerol is preferable.

As part of our ongoing interest in the development of new catalytic methods that enable controlled and selective transformations of highly functionalized bio-derived feedstocks, we recently discovered an efficient heterogeneous catalytic system for the direct conversion of bio-derived aqueous levulinic acid/FA streams to γ-valerolactone, catalyzed by ZrO_2-supported high-dispersed Au nanoparticles (NPs), in which high performance of the supported Au NPs for in situ generation of H_2 gas via selective FA decomposition under mild conditions is essential [18]. This Au/ZrO_2-FA protocol is also a suitable method for selective hydrogenolysis of glycerol to 1,2-PDO in high yields. However, the high cost and limited availability of Au have necessitated the development of earth-abundant base-metal alternatives for these applications. Simple Cu-based catalysts are promising candidates because they have high activities toward FA decomposition in the vapor phase [19–22]. Moreover, it is also well established that Cu catalysts are very selective for catalytic hydrogenolysis of glycerol under a H_2 atmosphere [23,24]. In this paper, we report that a simple Cu–Zr nanocomposite featuring high component dispersion can be used as an efficient catalyst in the selective conversion of glycerol to 1,2-PDO using bio-derived FA as a convenient H_2 source.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared using the conditions and methods listed in Table 1.

2.1.1. Oxalate gel (OG) coprecipitation (CP) method [25].

Briefly, an alcoholic solution of 20% excess oxalic acid was injected rapidly into an alcoholic solution of zirconium (cerium) nitrate (0.1 mol/L) containing the desired amount of copper (iron, cobalt, nickel) nitrate at room temperature under vigorous stirring. After stirring for 2 h, the resultant gel-like precipitates were separated by filtration, followed by air drying at 110 °C overnight. The as-obtained materials were then calcined in a muffle oven at 500 °C for 4 h.

2.1.2. Na_2CO_3 CP method

Typically, a mixed aqueous solution of copper nitrate and zinc nitrate (each 0.1 mol/L) and a solution of Na_2CO_3 (0.1 mol/L) were added slowly and simultaneously to 150 mL of deionized water at 80 °C under vigorous stirring. The pH was kept constant at 6.5–7.0. After stirring for 4 h, the precipitates were separated by filtration, followed by drying at 110 °C overnight. The as-obtained material was then calcined in a muffle oven at 500 °C for 4 h.

2.1.3. Incipient wetness impregnation (Imp) method

In a typical procedure, a certain amount of ZrO_2 support or SiO_2 support was soaked in an aqueous solution of copper nitrate of appropriate concentration. The mixture was stirred for 4 h at room temperature and then stirred at 85 °C until the mixture was dry. The samples were dried in an oven at 110 °C overnight.

2.1.4. Urea deposition-precipitation (urea DP) method

Typically, a mixed aqueous solution of copper nitrate (0.1 mol/L) and urea (10 mol/L), and ZrO_2 (or P25) were added to 200 mL of deionized water at 90 °C under vigorous stirring for 4 h. The solids were separated by filtration, followed by drying in an oven at 110 °C overnight. The as-obtained materials were

Table 1

FA conversions and CO contents for different catalysts.

Catalyst	Preparation method	FA conversion [a] (%)	CO concentration [b] (ppm)
Cu/ZnO-Al_2O_3 [c]	Na_2CO_3 CP	7	5
30%Cu/ZnO-Al_2O_3	Na_2CO_3 CP	9	11
30%Cu/ZnO	Na_2CO_3 CP	15	47
30%Fe/ZrO_2	OG CP	1	45
30%Co/ZrO_2	OG CP	1	57
30%Ni/ZrO_2	OG CP	2	55
30%Cu/SiO_2	Imp	1	50
30%Cu/CeO_2	OG CP	20	32
30%Cu/TiO_2	Urea DP	5	30
30%Cu/ZrO_2	Urea DP	10	40
30%Cu/ZrO_2	Imp	1	52
30%Cu/ZrO_2	OG CP	50	12

Reaction conditions: FA 18 mmol, H_2O 40 mL, n_{FA}/n_{metal} = 24, 160 °C, 5 h.
[a] Analyzed by a HPLC (HP 1100, Agilent, USA) equipped with a refractive index detector (RID) and a Platisil ODS C18 column.
[b] Measured by using a GC analysis system equipped with a methanizer and a flame ionization detector (detection limit ~1.0 ppmv).
[c] Supplied by Research Institute of Nanjing Chemical Industrial Group.