Catalysis Today 212 (2013) 120–126

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrogenolysis of glycerol to 1,3-propanediol over bifunctional catalysts containing Pt and heteropolyacids

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ARTICLE INFO

Article history:
Received 11 March 2012
Received in revised form 27 June 2012
Accepted 2 September 2012
Available online 18 October 2012

Keywords:
Glycerol
Hydrogenolysis
1,3-Propanediol
Heteropolyacids

ABSTRACT

Hydrogenolysis of glycerol to 1,3-propanediol was conducted over zirconia supported bifunctional catalysts containing Pt and heteropolyacids using $H_4SiW_{12}O_{40}$ (HSiW), $H_3PW_{12}O_{40}$ (HPW) and $H_3PMo_{12}O_{40}$ (HPMo) as active compounds. Pt/ZrO_2 was also examined for comparison. The as-prepared catalysts were characterized by BET, CO chemisorption, XRD, Raman spectra, NH_3-TPD and FTIR of adsorbed pyridine. Compared with Pt/ZrO_2, heteropolyacids modified Pt/ZrO_2 catalysts showed higher acidity and better catalytic performance of glycerol hydrogenolysis to 1,3-propanediol. Among them, Pt-HSiW/ZrO_2 exhibited superior performance due to the high Brønsted acid sites and good thermal stability. Independent of the heteropolyacid type, the concentration of Brønsted acid sites appeared as a key to the selective formation of 1,3-propanediol from glycerol hydrogenolysis, whereas the concentration of Lewis acid sites was related to the formation of 1,2-propanediol. We also investigated the reaction network and proposed a possible reaction pathway.

1. Introduction

The catalytic transformation of biomass-derived feedstocks for the synthesis of value-added fuels, chemicals and materials has been attracting much attention, due to the diminishing reserves and rising price of fossil resources [1,2]. Recent development of biodiesel production by transesterification of plant oils and animal fat has made a large amount of glycerol available as a renewable feedstock for the production of various fuels and valuable chemicals [2–5]. Significant research efforts have been focused on the conversion of glycerol by various catalytic processes such as reforming, oxidation, dehydration, hydrogenolysis, etherification, esterification and so on [3–10].

Hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO) is a noticeable pathway due to its production of renewable value-added chemicals. 1,3-PDO owes much higher economical value than 1,2-PDO, in particular, as an important monomer in the synthesis of polyester fibers [4,5,11]. Industrial production of 1,3-PDO is currently based on chemical synthesis via hydration of acrolein or hydroformylation of ethylene oxide [12]. The development of an alternative environmentally benign process for the production of 1,3-PDO based on the biomass-derived glycerol as a sustainable feedstock is a real challenge.

Supported Ir, Pt, Ru, Rh, Pd and Cu catalysts have been used for glycerol hydrogenolysis to 1,3-PDO [9,10,13–21]. Among these catalysts, supported Pt catalysts are more selective for this reaction than others. To obtain 1,3-PDO effectively, it is necessary to add acid component to the catalysts due to the bi-functional mechanism. Previous research [9,22] shows that hydrogenolysis of glycerol to 1,3-PDO proceeds via dehydration of glycerol to 3-hydroxypropaldehyde (3-HPA) followed by hydrogenation. According to the above mechanism, acid catalysts play an important role in glycerol hydrogenolysis. Various acid catalysts including H_2WO_4, H_2SO_4, sulfated zirconia, WO_3/ZrO_2, and $WO_3/TiO_2/SiO_2$ have been used [9,10,18,21,23,24]. Studies by Chaminand et al. [23] showed that hydrogenolysis of glycerol to 1,3-PDO on Rh/SiO_2 catalyst achieved 4% yield in the presence of H_2WO_4 at 200 °C and 8.0 MPa. Tomishige and co-workers [18] reported that the yield of 1,3-PDO reached 38% over Ir-ReO_x/SiO_2 catalyst with H_2SO_4 as an additive in a batch reactor. However, the liquid acids would cause several problems in terms of catalyst separation, reactor corrosion and environmental protection. Recently, Oh et al. [24] have communicated the use of Pt-sulfated zirconia with 1,3-dimethyl-2-imidazolidinone in glycerol hydrogenolysis but such strong acidic

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http://dx.doi.org/10.1016/j.cattod.2012.09.011

catalysts deactivate quickly as carbonaceous deposits block the catalyst surface. Additionally, the usage of organic solvent will greatly reduce the environmental and economical viability.

Heteropolyacids (HPAs) have demonstrated to display outstanding catalytic performance for both homogeneous and heterogeneous acid-catalyzed reactions because of its well-defined structure and widely tunable acidity [8,25–27]. HPAs possess unique physicochemical properties, with their structural mobility and multifunctionality, which is useful in industrial processes such as the liquid–phase dehydration of alcohols and hydration of esters or olefins [26–28]. Additionally, heterogeneous acid catalysis by HPAs has attracted much interest due to its potential of great economic rewards and green benefits. Compared to conventional solid acid catalysts such as oxides and zeolites, HPAs possess strong acidity, uniform acid sites and easily tunable acidity. Generally, tungsten HPAs owns stronger acidity, higher thermal stability and lower oxidation potential than molybdenum HPAs, which makes tungsten HPAs used more widely [29]. However, HPAs lack thermal stability and leach easily in polar solvents. To solve this problem, HPAs are often immobilized on supports such as SiO_2 or ZrO_2. Kozhevnikov and co-workers [27] have studied the interaction between HPW and support with ammonia adsorption calorimetry, MAS NMR and FTIR and suggested increasing interaction in the following order: $SiO_2 < TiO_2 < Nb_2O_5 < ZrO_2$. Moreover, our previous study [13] showed that the Pt-HSiW/ZrO_2 catalyst was rather durable during one-step hydrogenolysis of glycerol to biopropanols. Taken together, it is worthwhile to study supported HPAs as acid catalysts for glycerol hydrogenolysis.

In the present investigation, several zirconia supported Pt-HPAs (HSiW, HPW and HPMo) bi-functional catalysts were prepared, characterized, and tested in aqueous solution for glycerol hydrogenolysis. Special emphasis was also laid on formation route of glycerol hydrogenolysis and degradation based on the catalytic performance in the reaction of products and detected intermediates.

2. Experimental

2.1. Catalyst preparation

ZrO_2 (Jiangsu Qianye Co., Ltd., China) was used as support of the catalysts. $H_2PtCl_6{\cdot}6H_2O$ (AR), HSiW (AR), HPW (AR) and HPMo (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the catalysts were prepared by incipient wetness impregnation method. Typical procedures for the preparation of Pt-HSiW/ZrO_2 catalyst are as follows. The Pt/ZrO_2 catalyst was prepared by impregnation of zirconia support with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$. The impregnated sample was dried overnight at 110 °C and then calcined at 400 °C in static air for 4 h. After impregnated HSiW onto Pt/ZrO_2, Pt-HSiW/ZrO_2 was dried overnight at 110 °C and then calcined at 350 °C in static air for 4 h. Pt-HPW/ZrO_2 and Pt-HPMo/ZrO_2 were prepared in the similar way to that of Pt-HSiW/ZrO_2. The Pt and HPAs loadings were fixed at 2 wt.% and 15 wt.%, respectively.

2.2. Catalyst characterization

N_2 adsorption–desorption isotherms were recorded at −196 °C using a Micromeritics ASAP 2420 instrument after degassing at 300 °C for 8 h in vacuum. BET surface area and BJH pore size distribution were calculated by desorption isotherms.

CO chemisorption was measured at 50 °C in Auto Chem. 2920 equipment (Mircromeritics, USA). Prior to the measurement, about 0.2 g catalyst sample was first reduced in situ for 2 h in pure H_2 at 200 °C, then purged with He at the same temperature for 1 h and finally cooled down to 50 °C. The CO chemisorption was operated by pulse injection of pure CO at 50 °C. The Pt particle size was calculated by assuming an adsorption of one CO molecule per surface platinum atom.

Powder X-ray diffraction (XRD) patterns were conducted at room temperature on a D2/max-RA X-ray diffractometer (Bruker, Germany) using Cu Kα radiation at 30 kV and 10 mA. The X-ray patterns were recorded in 2θ values ranging from 10° to 90° at the scanning rate of 5°/min.

Raman spectra were recorded with a LabRAM HR800 System equipped with a CCD detector at room temperature. The 325 nm of the He-Cd laser was used as the exciting source with a power of 30 MW.

NH_3-TPD was carried out in the same apparatus as CO chemisorption. Prior to each run, the catalyst sample (0.3 g) was pretreated in He at 350 °C for 1 h, then cooled to 100 °C and was saturated with pure NH_3 for 30 min. After being purged with He for 30 min, the sample was heated to 700 °C at a heating rate of 10 °C/min and the NH_3 desorption was monitored with a TCD detector.

To evaluate and analyze the nature and acid amount of catalysts, FTIR spectra of adsorbed pyridine (Py-IR) of solid samples were carried out on a VERTEX70 (Bruker) FT-IR spectrophotometer, equipped with a deuterium triglycine sulphate (DTGS) detector. Prior to pyridine adsorption, the samples were heated to 300 °C under vacuum, and then cooled to 30 °C. The Py-IR spectra were then recorded at 200 °C after applying vacuum for 30 min. The quantitative calculation of Brønsted and Lewis acid sites was determined by the integrated area of the adsorption bands at about 1540 and 1450 cm^{-1}, respectively. The acidity of Brønsted and Lewis acid sites was calculated by using the adsorption coefficient values reported in the previous paper [30].

2.3. Catalytic tests

Hydrogenolysis of glycerol was conducted in a vertical fixed-bed reactor (i.d. 12 mm, length 600 mm) with an ice-water trap. In a typical run, 2.0 g catalyst (20–40 mesh) was charged in the constant temperature section of the reactor, with quartz sand packed in both ends. Prior to the test, the catalyst sample was in situ reduced in a stream of pure H_2 (100 ml/min) at 200 °C for 2 h. After reduction, the system was cooled to the desired temperature. A 10 wt.% glycerol aqueous solution was fed continuously into the reactor with an HPLC pump along with a co-feed H_2 of gas flowing at 100 $cm^3\ min^{-1}$. The liquid and gas products were cooled and collected in a gas–liquid separator immersed in an ice-water trap. The products were obtained when the reaction reached the steady state. Additionally, the reaction performance of 1,3-PDO, 1,2-PDO and ethylene glycol (EG) was also evaluated in order to reveal the reaction pathway of glycerol hydrogenolysis.

The liquid products were analyzed by gas chromatography using a capillary column (DB-WAX, 30 m × 0.32 mm) equipped with a FID detector. The tail gas was off-line analyzed by a gas chromatography with a capillary column (OV-101, 60 m × 0.25 mm) and a TCD detector. The products obtained were also identified by GC–MS. The conversion of glycerol and selectivity of products were calculated as follows:

$$\text{Conversion}\,(\%) = \frac{\text{moles of glycerol (in)} - \text{moles of glycerol (out)}}{\text{moles of glycerol (in)}} \times 100$$

$$\text{Selectivity}\,(\%) = \frac{\text{moles of one product}}{\text{moles of all products}} \times 100.$$