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Promoting effect of WO_x on selective hydrogenolysis of glycerol to 1,3-propanediol over bifunctional Pt–WO_x/Al_2O_3 catalysts

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ABSTRACT

Despite 1,3-propanediol possessing high economic value, its production from glycerol hydrogenolysis is a challenging task. Herein, a series of WO_x promoted Pt/Al_2O_3 catalysts with various WO_x contents were prepared and investigated for selective production 1,3-propanediol from glycerol hydrogenolysis. To explore the structure feature, these catalysts were fully characterized by BET, CO chemisorption, HRTEM, XRD (*in situ* XRD), Raman, NH_3–TPD, Py–IR, H_2–TPR, and XPS. Among them, Pt–10WO_x/Al_2O_3 achieved the highest 1,3-propanediol yield up to 42.4%, which was ascribed to the large concentration of Brønsted acid sites, strong electronic interaction between Pt with WO_x and hydrogen spillover. The strong correlation between 1,3-propanediol yield and Brønsted acid site indicated its essential role for the formation of 1,3-propanediol. Meanwhile the linear correlation between 1,2-propanediol yield and Lewis acid site gave direct evidence that Lewis acid site preferentially generated 1,2-propanediol.

1. Introduction

The use of renewable resources as feedstocks for the production of fuels, chemicals and materials has been attracting much attention, as the fossil resources will be exhausted in a few decades [1,2]. In this context, biomass is a desirable candidate as an alternative and carbon neutral resource. As a biomass-derivative, glycerol is currently produced in a large amount as a by-product in manufacturing biodiesel by transesterification of vegetable oils with methanol or ethanol [3]. Therefore, it is urgent to effectively utilize the renewable glycerol for the sustainable development of biodiesel industry. Significant research efforts have been focused on the transformation of glycerol by various catalytic processes, such as reforming [4], oxidation [5], dehydration [6], hydrogenolysis [7,8], esterification [9,10] and polymerization [11].

The catalytic hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO), which are widely used as versatile specialty chemicals, is quite promising. 1,3-PDO owes much higher economic value than 1,2-PDO, in particular, as an important monomer in the synthesis of polyester fibers [7]. Conversion of glycerol to 1,2-PDO has been extensively studied, and high yields have been obtained in previous reports [12–15]. Our recent work has achieved 98.0% yield of 1,2-PDO over B_2O_3 modified Cu/SiO_2 catalyst [15]. On the contrary, the direct hydrogenolysis of glycerol to 1,3-PDO is still a challenging task. One of the key problems is concerned with the 1,3-PDO selectivity, which requires careful design of catalyst.

There have been several reports on homogeneous and heterogeneous catalysts for the catalytic hydrogenolysis of glycerol to 1,3-PDO [16–21]. Nevertheless, most of previous studies have been performed in organic solvent [16,19,22]. Considering that crude glycerol from biodiesel production contains water unavoidably and it is also a by-product of the reaction sequence, water is the desired solvent for glycerol hydrogenolysis from the standpoint of environmental and economic viability. Among them, the relatively effective processes using water primarily employed Ir–ReO_x/SiO_2 [20,23] or Pt-based catalysts modified by tungsten species (WO_3 [16,24], WO_x [21,25], H_2WO_4 [22] and $H_4SiW_{12}O_{40}$ [26,27]). Nakagawa et al. developed Ir–ReO_x/SiO_2 catalyst with H_2SO_4 as an additive in a batch reactor, over which the yield of 1,3-PDO reached 38% [20]. To overcome the corrosive liquid H_2SO_4, H-ZSM-5 was considered as the most suitable solid acid co-catalyst and the yield of 1,3-PDO declined to 33% moderately [23]. Zhang et al. [21] performed glycerol hydrogenolysis over mesoporous WO_3–TiO_2 with a loading of 2 wt% Pt at 180 °C and 5.5 MPa, which gave 40.3% 1,3-PDO selectivity and 24.2% conversion. Qin et al. [24] achieved 32.0% yield of 1,3-PDO over Pt/WO_3/ZrO_2 catalyst in glycerol hydrogenolysis at 130 °C and 4 MPa. The other relatively feasible catalysts included Pt/WO_3/TiO_2/SiO_2 [28], Pt-$H_4SiW_{12}O_{40}$/ZrO_2

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[27,29], $Pt/Al_2O_3 + H_4SiW_{12}O_{40}$ [26], Pt/WO_x/Boehmite [25], and $Pt/WO_x/SiO_2/ZrO_2$ [30]. These results show that the acidic tungsten species appear as a key to the selective formation of 1,3-PDO, but the role of tungsten species is still unclear. Despite growing experimental work, a systematic understanding remains unavailable on the type of acid sites in governing the rate and cleavage C—O bond selectively over tungsten-containing catalysts.

In the present work, we reported a detailed study for continuous hydrogenolysis of glycerol over Pt-WO_x/Al_2O_3 catalysts in aqueous media. A 42.4% yield of 1,3-PDO was achieved at 64.2% conversion, 160 °C and 5.0 MPa over Pt–$10WO_x/Al_2O_3$ catalyst. Special emphasis would be focused on the role of WO_x and structure-behavior correlation.

2. Experiment

2.1. Catalyst preparation

The Pt–WO_x/Al_2O_3 catalysts were prepared by sequential impregnation method. Specifically, γ-Al_2O_3 (China Research Institute of Daily Chemical Industry) was impregnated with aqueous solutions containing the desired amount of ammonium paratungstate (Sinopharm Chemical Reagent Co., Ltd., China, (SCRC)). These WO_x/Al_2O_3 samples were dried overnight at 110 °C and calcined at 600 °C in static air for 4 h. The Pt–WO_x/Al_2O_3 catalysts were fabricated by impregnation of WO_x/Al_2O_3 samples with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (SCRC). Impregnated samples were dried overnight at 110 °C and then calcined in static air at 400 °C for 4 h. According to the tungstate oxide mass (y in wt%, quantified in the form of WO_3), the final catalysts were designated as Pt–yWO_x/Al_2O_3 ($y = 5 \sim 20$). The Pt/Al_2O_3 without WO_x was also prepared as reference sample by impregnation of γ-Al_2O_3 with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$. The Pt/Al_2O_3 sample was dried and then calcined at 400 °C for 4 h. The loading of Pt were fixed at 2 wt% in all catalysts.

2.2. Catalyst characterization

N_2 adsorption–desorption isotherms were recorded at −196 °C on a Micromeritics ASAP 2420 instrument. Prior to the measurement, each sample was degassed under vacuum at 300 °C for 8 h.

Powder X-ray diffraction (XRD) patterns were collected on a D2/max-RA X-ray diffractometer (Bruker, Germany) with Cu Kα radiation operated at 30 kV and 10 mA. The X-ray patterns were recorded in 2θ values ranging from 10° to 90°. For *in situ* XRD measurement, these samples were flushed in pure H_2 at a flow rate of 30 $cm^3\ min^{-1}$ and heated from 30 °C to 150, 250, 300, 350, 400, 450, 500, 550 and 600 °C at a ramping rate of 5 °C min^{-1}. The XRD patterns were recorded after the preset temperature attained for 30 min.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the samples were obtained in JEM 2011F apparatus operating at 200 kV voltages. The samples after reduction were suspended in ethanol with an ultrasonic dispersion for 30 min and deposited on carbon-coated copper grids.

Raman spectroscopy was conducted on a LabRAM HR800 System using a CCD detector at room temperature. The 325 nm of the He–Cd laser was employed as the exciting source with a power of 30 MW.

CO chemisorption was performed in Auto Chem. II 2920 equipment (Mircromeritics, USA). Prior to adsorption measurement, 0.2 g catalyst sample was reduced in H_2 for 2 h at 200 °C and then flushed with He for 1 h followed by cooling down to 30 °C. The CO chemisorption was measured by pulse injection of pure CO at 30 °C. The Pt particle size was determined by assuming that the stoichiometry of adsorbed CO molecule to surface platinum atom was one.

Temperature-programmed reduction of hydrogen (H_2–TPR) was conducted in the same apparatus as CO chemisorption. For each run, about 0.10 g sample was firstly pretreated in Ar at 150 °C for 30 min and then cooled to 30 °C. After that, 10% H_2 diluted in Ar was introduced into the system and a cold trap of 2-propanol-liquid nitrogen slurry was provided to condense the water gas. The sample was heated up to 900 °C at a ramp of 10 °C/min and simultaneously recorded by a thermal conductivity detector.

Temperature-programmed desorption of ammonia (NH_3–TPD) was measured in the same apparatus as CO chemisorption. At first, 0.3 g catalyst sample was pretreated in He at 400 °C for 1 h and then cooled to 100 °C followed by saturating with pure NH_3 for 30 min. Finally, the sample was heated to 600 °C at a ramping rate of 10 °C/min and the desorbed NH_3 was monitored with a MS detector (Agilent, USA).

IR spectra of adsorbed pyridine (Py–IR) were performed in Vertex 70 (Bruker) FT-IR spectrophotometer with a deuterium triglycine sulfate (DTGS) detector. For each run, the sample was pressed into self-supporting wafers and degassed in vacuum at 300 °C for 1 h followed by exposure to pyridine vapor. Subsequently, the Py–IR spectra were measured at 200 °C after applying vacuum for 30 min. The quantification of Brønsted and Lewis acid sites was estimated from the integrated area of adsorption bands at *ca.* 1540 and 1450 cm^{-1}, respectively, described elaborately in our previous reports [10,27].

X-ray photoelectron spectroscopy (XPS) was carried out on a VG MiltiLab 2000 spectrometer with Mg Kα radiation and a multichannel detector. The catalyst was reduced in flowing hydrogen at 200 °C for 2 h before the measurement. The obtained binding energy values were calibrated by the C 1s peak at 284.6 eV.

2.3. Catalytic reaction

The catalytic test was performed in a vertical fixed-bed stainless steel reactor with an ice–water trap. Typically, 2.0 g catalyst (20–40 mesh) was placed into the constant temperature section of the reactor possessing quartz sand to fix it in both ends. Prior to the test, the catalyst was reduced in flowing H_2 (100 ml/min) at 200 °C for 2 h. Subsequently, a glycerol aqueous solution (1.8 ml/h) was continuously pumped into the reactor inlet through an HPLC pump. The liquid and gas products were condensed and collected in a gas–liquid separator immersed in an ice–water trap. The standard reaction conditions were as follows: 160 °C, 5.0 MPa, 10 wt% glycerol aqueous solution, H_2/glycerol = 137:1 (molar ratio), WHSV = 0.09 h^{-1}.

The liquid products were analyzed by a gas chromatography (Ruihong chromatogram analysis Co., Ltd., China) with a FID using a DB-WAX capillary column. The outlet gas was off-line analyzed using a gas chromatograph (Huaai chromatogram analysis Co., Ltd., China) equipped with a TCD and OV-101 column. Concurrently, the assignment of the products was identified by GC–MS (Agilent, USA).

The identified products were 1,3-PDO, 1,2-PDO, 1-propanol (1-PO), 2-propanol (2-PO), ethanol, acetol, propionic acid, acetic acid, ethylene glycol, methanol, propane, methane and CO_2. The conversion of glycerol and selectivity of products were calculated using the following expressions:

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

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