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# $SiO_2$ promoted $Pt/WO_x/ZrO_2$ catalysts for the selective hydrogenolysis of glycerol to 1,3-propanediol

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## ABSTRACT

To improve 1,3-propanediol selectivity, a series of $SiO_2$ modified $Pt/WO_x/ZrO_2$ catalysts with various $SiO_2$ content for glycerol hydrogenolysis were prepared via deposition–precipitation method followed by sequential impregnation. These catalysts were systematically characterized using BET, ICP, CO chemisorption, XRD, $H_2$-TPR, $NH_3$-TPD, Raman, IR, TEM and XPS. The incorporation of suitable $SiO_2$ into $Pt/WO_x/ZrO_2$ catalysts had extremely favorable effects on the dispersion of $WO_x$ and transformation from crystalline $WO_3$ to active polytungstate, while superfluous $SiO_2$ converted polytungstate to monotungstate. Among them, the 5PtW/ZrSi catalyst reached superior activity and maximum 1,3-propanediol selectivity, up to 52.0%. The structure-activity correlation indicated that glycerol hydrogenolysis conformed to dehydration–hydrogenation reaction mechanism and found that Pt and polytungstate were the most active species.

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## 1. Introduction

Renewable resources are attracting more and more attention as alternative raw materials for the synthesis of value-added fuels, chemicals and materials [1,2]. Among them, glycerol has gained considerable interest due to its available production in huge amounts from biodiesel process and capability to produce valued-added products [3]. Nowadays, significant work has been dedicated to the valorization of glycerol by several catalytic processes including dehydration [4], hydrogenolysis [5,6], reforming [7], esterification [8,9] and oxidation [10]. In this context, hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO) is considered as a promising approach for their versatile application as important monomer for the production of polyester fibers.

Significant efforts have been focused on glycerol hydrogenolysis to 1,2-PDO, and remarkable advances have been achieved in some literature [11–14]. Our recent work [11] has presented up to 98.0% yield of 1,2-PDO over $B_2O_3$ modified $Cu/SiO_2$ catalyst and found the structure-sensitive feature of glycerol hydrogenolysis. In comparison with 1,2-PDO, 1,3-PDO owns much higher economic value while there are only few reports available on the potential utilization of glycerol for the synthesis of 1,3-PDO. Industrial production of 1,3-PDO is currently on the basis of petroleum route by hydroformylation of ethylene oxide or hydration of acrolein [15]. Nevertheless, selective production 1,3-PDO from biomass-derived glycerol is still a challenge, particularly without high boiling-point organic solvent or acidic additives [16]. It is supposed that the secondary hydroxyl group of glycerol is less accessible to active sites than the primary one because of the steric hindrance effect, which results in low selectivity to 1,3-PDO [17].

It is well-established that crude glycerol from biodiesel process contains water and hydrogenolysis of glycerol leads to an unavoidable accumulation of by-product water, which makes water the preferred solvent in terms of environmental and economic viability. Right now, the relatively effective hydrogenolysis processes using water as solvent mainly employed $Ir–ReO_x/SiO_2$ [18,19] or platinum-based catalysts combined with tungsten species [15,16,20–25]. Tomishige and co-workers [18,19] developed $Ir–ReO_x/SiO_2$ catalyst for glycerol hydrogenolysis using liquid $H_2SO_4$ as co-catalyst; the 1,3-propanediol yield was up to 38%. Nevertheless, the inherent disadvantage of corrosive $H_2SO_4$ greatly hinders to exploit proper reaction technology involving reactor

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and product separation system. Accordingly, alternative heterogeneous solid acid catalyst is highly desirable for practical application. Very recently, we have reported a continuous process for glycerol hydrogenolysis to 1,3-PDO over $ZrO_2$ or $SiO_2$ supported Pt-silicotungstic acid bifunctional catalysts, but these catalysts suffered from deactivation and showed low selectivity [15,24,25]. Kurosaka et al. [16] produced 1,3-PDO by hydrogenolysis of glycerol over $Pt/WO_x/ZrO_2$ catalyst for the first time; the 1,3-PDO yield was up to 24%. However, employing organic solvent 1,3-dimethyl-2-imidazolidinone limited its wide application. Qin et al. [21] exhibited the transformation of glycerol to 1,3-PDO with 45.6% selectivity over $Pt/WO_x/ZrO_2$ catalyst using water as solvent, which provided a sustainable and facile reaction system. To the best of our knowledge, no extensive researches of the $Pt/WO_x/ZrO_2$ catalysts have been reported on the structure-activity relationship for glycerol hydrogenolysis so far. Additionally, the unique role of $WO_x$ species is still not clear for this reaction.

$WO_x/ZrO_2$ or $Pt/WO_x/ZrO_2$ catalysts have been widely investigated and presented excellent reactivity in a variety of reaction processes due to their strong acidity, higher thermal and chemical stability [26–29]. Moreover, a number of additives including $In_2O_3$ [30], Fe [31], $CeO_2$ [32], $CuO_x$ [33] and $Al_2O_3$ [34] have been employed to modify the acidic and electronic properties. Recently, Lauriol-Garbey et al. [4] have communicated that the acrolein selectivity for glycerol dehydration can be improved over $WO_x/ZrO_2$ by doping with $SiO_2$. The addition of $SiO_2$ has marked influence on the textural and acidic properties of $WO_3/ZrO_2$. Appropriate acidity and good dispersion of active metal are indispensable for glycerol hydrogenolysis based on dehydration–hydrogenation bifunctional mechanism, as clarified by our previous reports [24,25]. Nevertheless, no literature have been published regarding structure-performance correlation of $SiO_2$ modified $Pt/WO_x/ZrO_2$ catalysts for glycerol hydrogenolysis. Therefore, the $SiO_2$ modulated $Pt/WO_x/ZrO_2$ as potential catalysts for chemoselective hydrogenolysis of glycerol to 1,3-PDO was explored without using organic solvent. These as-prepared catalysts were fully characterized by various techniques involving BET, ICP, CO chemisorption, XRD, $H_2$-TPR, $NH_3$-TPD, Raman, IR, TEM and XPS. The unique role of $WO_x$ and structure–activity relationship of these $SiO_2$ doped $Pt/WO_x/ZrO_2$ catalysts in glycerol hydrogenolysis was also discussed in detail.

## 2. Experimental

### 2.1. Catalyst preparation

The $SiO_2$ doped $ZrO_2$ samples were prepared by deposition–precipitation method. Firstly, a 0.5 mol/L $Zr(NO_3)_4{\cdot}3H_2O$ (Sinopharm Chemical Reagent Co., Ltd, China (SCRC)) aqueous solution mixed with the desired colloidal silica aqueous solution ($SiO_2$, 30 wt.%, Qingdao Ocean Chemical CO., Ltd, China) under vigorous stirring. Then, a 28 wt.% ammonia (SCRC) aqueous solution was dripped into it at 80 °C until the pH was attained to 9. The mixture was aged at 80 °C for 2 h, filtrated and washed with hot deionized water for 5 times. Finally, these precipitate was dried at 110 °C overnight and then calcined at 600 °C in static air for 4 h.

These $SiO_2$ doped $ZrO_2$ samples were impregnated with an aqueous solution containing the desired amount of ammonium paratungstate (SCRC). After impregnation, these samples were dried overnight at 110 °C and then calcined at 600 °C in static air for 4 h. The above samples were further impregnated 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. The obtained catalysts are designated as *x*PtW/ZrSi, where the *x* (wt.%) represents $SiO_2$ nominal mass loading in the $SiO_2$-$ZrO_2$ mixed support. In all catalysts the nominal weight loading of Pt and $WO_x$ (quantified in the form of $WO_3$) were fixed at 2 wt.% and 15 wt.%, respectively.

### 2.2. Catalyst characterization

$N_2$ adsorption–desorption isotherms were performed at −196 °C on a Micromeritics ASAP 2420 instrument. These samples were first degassed under vacuum at 300 °C for 8 h.

ICP optimal emission spectroscopy (Optima2100DV, PerkinElmer) was employed to determine the compositions of as-prepared catalysts.

Powder X-ray diffraction (XRD) patterns were carried out on a D2/max-RA X-ray diffractometer (Bruker, Germany) with Cu $K\alpha$ radiation. The X-ray patterns were measured in $2\theta$ values in the range from 10° to 90° at a 5° $min^{-1}$ scan speed.

CO chemisorption was conducted in Auto Chem.II2920 equipment (Mircromeritics, USA). For each run, 0.2 g catalyst sample was placed in a quartz tube and reduced in $H_2$ for 2 h at 200 °C. After that, the sample was flushed with He for 1 h, cooled down to 50 °C and then pulse injected pure CO. The Pt dispersion 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 carried out in the same apparatus as above. For each run, about 0.1 g sample was placed into a *U*-shaped quartz tube and pretreated in Ar at 300 °C for 30 min and then cooled to 50 °C. After that, a 10 vol% $H_2$–Ar mixed gas was employed and a cold trap with isopropanol–liquid nitrogen slurry was used to condense the water vapor. The $H_2$-TPR was started from 50 °C to 1000 °C at a ramp of 5 °C/min and simultaneously monitored by a thermal conductivity detector (TCD).

Temperature-programmed desorption of ammonia ($NH_3$-TPD) was performed 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. Subsequently, the sample was heated to 700 °C at a rate of 5 °C/min and the desorbed $NH_3$ was monitored with a MS (Agilent, USA).

Raman spectroscopy was recorded 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.

FTIR spectra were conducted on a Vertex 70 (Bruker) FT-IR spectrophotometer with a deuterium triglycine sulfate (DTGS) detector. The powder samples were mixed with KBr (2 wt.%) and pressed into translucent disks at room temperature.

TEM measurement was carried out on a field-emission transmission electron microscopy (FETEM, JEM-2011F) operating at 200 kV voltages. The reduced samples were suspended in ethanol with an ultrasonic dispersion for 30 min and deposited on carbon-coated copper grids.

X-ray photoelectron spectroscopy (XPS) were performed on a VG MiltiLab 2000 spectrometer with Mg $K\alpha$ radiation and a multichannel detector. Prior to each test, the calcined sample was reduced in $H_2$ at 200 °C for 2 h. The binding energies were referenced using the C1s peak at 284.6 eV. The experiment error was given within ±0.1 eV.

### 2.3. Catalytic reaction

Glycerol hydrogenolysis tests were conducted in a vertical fixed-bed stainless steel reactor (12 mm of inner diameter, length of 600 mm). Typically, 3.0 g catalyst (20–40 mesh) was loaded in the constant temperature section of the reactor with quartz sand packed in both ends. Prior to the reaction, the sample was prereduced in flowing $H_2$ (100 mL/min) at 200 °C for 2 h. Subsequently,

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