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# Promoting effect of rhenium on catalytic performance of Ru catalysts in hydrogenolysis of glycerol to propanediol

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ABSTRACT

$Ru/Al_2O_3$, Ru/C and $Ru/ZrO_2$ catalysts were applied to the hydrogenolysis of glycerol to propanediol, and the effect of Re as an additive on the catalytic performance of Ru catalysts was examined. The catalyst systems were characterized by $N_2$ adsorption/desorption, XRD, TEM-EDX and XPS. The hydrogenolysis of glycerol was carried out under the conditions of 120–180 °C, 4–10 MPa hydrogen pressure and 4–8 h, and the conversion of glycerol varied from 18.7% to 29.7% over $Ru/Al_2O_3$, Ru/C and $Ru/ZrO_2$ catalysts. The reaction results indicate that Re possesses high promoting effect on the catalytic performance of Ru catalysts in glycerol hydrogenolysis.

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## 1. Introduction

Bio-diesel is described as an ideal alternative diesel fuel because it is a kind of environment friendly fuel and it makes a certain contribution to gaining energy sustainability. As it can be seen in Scheme 1, glycerol, as a byproduct of the transesterification of plant oils and methanol, will be surplus to a great extent accompanying the increase of bio-diesel production. However, the traditional usages of glycerol cannot meet with the high yield of glycerol produced from bio-resource. Therefore, the new usages of glycerol are being quested widely.

The conversions of glycerol to other chemicals include several routes, such as to acraldehyde, propanediol and glyceric acid and so on. Acraldehyde and propanediol are usually produced from petroleum derivatives [1–6]. Glyceric acid is used as an important medicinal intermediate [7–10]. Propanediol, both 1,2-propanediol and 1,3-propanediol, can be used as solvents and additives in many fields. Especially, 1,3-propanediol has attracted lots of attention because it can be used as the reactant of new polyester, PTT, which possesses unique and excellent properties.

It has been reported that propanediol can be produced through the catalytic conversion of glycerol (Scheme 2) [3–6]. Chaminand et al. [5] compared the catalytic performance of CuO/ZnO, Pd/C and Rh/C in the hydrogenolysis of glycerol, and 19% conversion of glycerol and 100% selectivity to 1,2-propanediol were obtained over CuO/ZnO catalyst, but no 1,3-propanediol was formed. When the reaction was carried out over rhodium catalysts combined with tungstic acid, the selectivity of 1,3-propanediol was improved [5]. Miyazawa et al. [3] found that the combination of Ru/C and Amberlyst resin was effective for the glycerol hydrogenolysis to 1,2-propanediol, compared with the combinations of the other noble metal catalysts (Rh/C, Pt/C and Pd/C) and acid promoters (Amberlyst resins, $H_2SO_4$, and HCl). Therefore, Ru was considered to be an effective catalytic component in glycerol hydrogenolysis [3,4]. However, from the results reported in the literatures [3–6], it can be seen that the activity and selectivity for the glycerol hydrogenolysis to propanediol with Ru catalysts alone are still not satisfying. Therefore, modification of Ru catalysts for improving their performance in the hydrogenolysis of glycerol is necessary. Maris et al. applied bimetallic PtRu/C and AuRu/C catalysts to the aqueous-phase hydrogenolysis of glycerol at 473 K and 40 bar $H_2$ and found that the PtRu catalyst appeared to be stable under the aqueous-phase reaction conditions, whereas the AuRu catalyst was altered by the harsh conditions [11]. Our research objective is to develop novel Ru-based bimetallic catalysts with high activity and selectivity for the hydrogenolysis of glycerol to propanediol under mild reaction condition, and to further make the working mechanism clear for the Ru-based bimetallic catalysts in the hydrogenolysis of glycerol through a series of investigations. Recently, we found a promotion effect of rhenium, as an additive, in Ru catalyzed system on the hydrogenolysis of glycerol to propanediols. In this paper, we report the results of glycerol hydrogenolysis over Ru/support + Re (using $Re_2(CO)_{10}$ as a precursor) catalytic system

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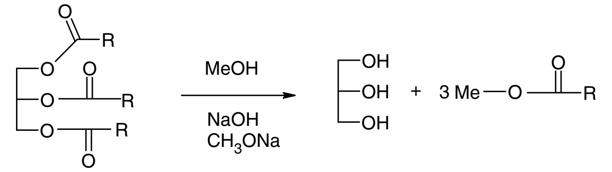
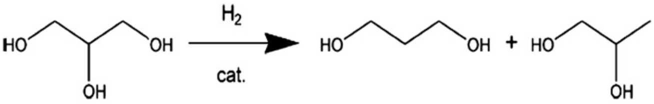


**Scheme 1.** Trasesterification reaction of plant oils.



**Scheme 2.** Hydrogenolysis of glycerol to propanediol.

and the effects of reaction conditions on the conversion and selectivities in the hydrogenolysis of glycerol.

## 2. Experimental

### 2.1. General comments

$ZrO(NO_3)_2$ (analytic pure) was purchased from Beijing Chemical Reagent Company and used as the starting material of $ZrO_2$. The 5%$Ru/Al_2O_3$ and 5%Ru/C catalysts were purchased from Alfa Aesar Company and used as received. $RuCl_3 \cdot 4H_2O$ was purchased from ShenYang Youse Jinshu Yanjiusuo and used for preparing $Ru/ZrO_2$ catalyst. Glycerol (ultra pure), the reaction substrate, was purchased from Alfa Aesar Company and used as received. Other reagents were purchased from Beijing Chemical Reagent Company.

### 2.2. Catalyst preparation

$ZrO_2$ was prepared by precipitation method; 600 ml aqueous solution of $ZrO(NO_3)_2$ (0.16 M) and 600 ml ammonium aqueous solution (2.5 wt%) were added dropwise into a well-stirred 400 ml ammonium aqueous solution (2.5 wt%). The precipitate formed was collected by filtration and washed with deionized water until the filtered mother solution became neutral. The obtained gel was washed with 50 ml ethanol for three times to remove water. Then alcohol gel was dried in flowing nitrogen gas (20 ml/min) at 110 °C for 12 h and calcined at 550 °C for 5 h in flowing nitrogen gas (20 ml/min).

A supported Ru catalyst, $Ru/ZrO_2$, was prepared by impregnation of support powder with $RuCl_3 \cdot 4H_2O$ aqueous solution (0.01 M Ru). The loading of Ruthenium on $Ru/ZrO_2$ was 5 wt%. After impregnation and solvent removal by evaporation, the precursors were dried at 110 °C for12 h, and calcined at 350 °C in air for 4 h and finally reduced in hydrogen ($H_2/N_2 = 3/5$, 80 ml/min) atmosphere at 450 °C for 4 h, and finally passivated in a flowing of $CO_2/N_2$ gas ($CO_2/N_2 = 2/5$, 70 ml/min) for 12 h and stored in the desiccator. The commercial catalysts, 5%$Ru/Al_2O_3$ and 5%Ru/C, were used as received.

### 2.3. Characterization of catalysts

The specific surface areas of the catalysts and the $ZrO_2$ support were measured by $N_2$ adsorption/desorption with the BET method on a Micromeritics ASAP 2010 C analyzer. The phase structures of the catalysts were determined by X-Ray diffraction (XRD) with a Bruker D8 Advance X-Ray Powder Diffractometer with Cu K$\alpha$ ($\lambda = 0.15406$ nm). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera Scanning X-ray Microprobe of ULVAC-PHI Inc. The spectra were referenced with respect to C1s line at 284.8 eV. The fresh $Ru/ZrO_2$ (reduced and passivated sample) and the spent catalyst $Ru/ZrO_2 + Re_2(CO)_{10}$ (recovered after reaction) were used for the measurement of XPS.

The morphologies, microstructure and the particle sizes of $Ru/ZrO_2$, $Ru/Al_2O_3$ and Ru/C were characterized by high-resolution transmission electron microscopy (HR-TEM, JEM-2010 of JEOL) equipped with an energy dispersive X-ray detector (EDX). The accelerating voltage was 120 kV. The samples of $Ru/ZrO_2$, $Ru/Al_2O_3$ and Ru/C were ultrasonically dispersed in ethanol and deposited on a holey carbon copper grid before measurement.

### 2.4. Hydrogenolysis reaction of glycerol

The hydrogenolysis of glycerol was carried out in a stainless steel autoclave of 100 ml with a magnetic stirrer. A standard procedure was as follow, the substrate, 10 ml 40 wt% glycerol aqueous solution, and 150 mg supported catalyst were used in every run. The reaction conditions were 120 °C ~180 °C, 4.0–10.0 MPa hydrogen pressure and 4–16 h reaction time. The amount of promoter rhenium carbonyl was 24.2 mg (the mol ratio of Ru to Re = 1). After adding substrate, catalyst and magnetic stirrer into the autoclave, the autoclave was sealed and purged with hydrogen at 2.0 MPa for three times. After the purge, the autoclave was heated to a given temperature and then the pressure of $H_2$ in the autoclave was increased to a given value at the given temperature. After the reaction, the autoclave was cooled with an ice bath and then decompressed. After adding certain amount of diethylene glycol dimethyl ether, as an internal standard, into the reaction mixture in the autoclave, then the mixture was mixed homogeneously. The liquid and the solid catalyst in the mixture were separated by centrifugation and filtration. The products in liquid phase were analyzed qualitatively by GC–Mass (GCMS-QP2010, SHIMADZU Corporation) and analyzed quantitatively with a gas chromatography (Lunan-SP 6890, PEG2M, 30 m × 0.25 mm; FID detector). The products in gas phase was not quantitatively analyzed, but qualitatively checked with a GC (TDX-01, TCD).

The conversion in present study is denoted as "conversion of glycerol to liquid products" (shorted as conversion of glycerol, hereafter). The selectivity is denoted as "selectivity in liquid products" (shorted as selectivity, hereafter). The conversion of glycerol and the selectivity of each liquid product in all runs in present study were calculated based on the following equations

$$\text{Conversion of glycerol}\,(\%) = \frac{\text{Sum of C mol of all liquid products}}{\text{Added glycerol before reaction (C mol)}} \times 100.$$

$$\text{Selectivity}\,(\%) = \frac{\text{C mol of each liquid product}}{\text{Sum of C mol of all liquid products}} \times 100.$$

## 3. Results and discussion

The BET specific surface areas of the supports and the catalysts are listed in Table 1. The BET specific surface area ($S_{BET}$) of commercial catalysts, $Ru/Al_2O_3$ and Ru/C, were 142 $m^2/g$ and 795 $m^2/g$, respectively, while the specific surface area of $Ru/ZrO_2$ catalyst prepared in this study was much smaller than that of $Ru/Al_2O_3$ and Ru/C. The $Ru/ZrO_2$ showed 54 $m^2/g$ BET specific surface area, which was just smaller than that of support $ZrO_2$ (57 $m^2/g$).

The XRD patterns of Ru/C, $Ru/Al_2O_3$ and $Ru/ZrO_2$ are showed in Fig. 1 and Fig. 2. In the XRD profile of the commercial catalyst, $Ru/Al_2O_3$, very weak diffraction peaks of $RuO_2$ species ($2\theta = 28.09$, 34.32 and 54.05) were observed (Fig. 1), but no diffraction peak belonged to metallic Ru phase was observed. This was perhaps due to

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