



Short Communication

Basic oxide-supported Ru catalysts for liquid phase glycerol hydrogenolysis in an additive-free system



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ABSTRACT

Several basic oxide-supported Ru catalysts (Ru/CeO₂, Ru/La₂O₃ and Ru/MgO) were prepared and evaluated for the hydrogenolysis of glycerol. The Ru catalysts were characterized by inductively coupled plasma–atomic emission spectroscopy, nitrogen adsorption, powder X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. Ru/CeO₂ showed the best performance in the reaction, which is associated with its smaller metal particle size and the weak surface basicity feature of CeO₂. 1,2-Propanediol is obtained as the main product through a dehydrogenation–dehydration–hydrogenation mechanism. The oxidation product lactic acid can be formed by a Cannizzaro reaction from the pyruvaldehyde intermediate.

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1. Introduction

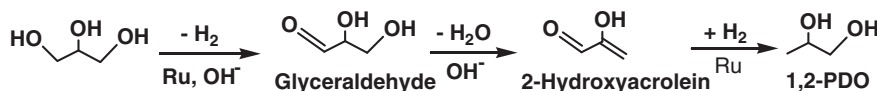
In recent years, because of the rapid development of biodiesel production by transesterification of vegetable oils or animal fats, large amounts of glycerol are available as a byproduct. How to utilize these biomass-derived glycerol has attracted great attention. In particular, the catalytic hydrogenolysis process is one of the most promising routes in the chemical transformation of glycerol. The main product arising from the hydrogenolysis of glycerol is 1,2-propanediol (1,2-PDO), which is extensively used as a monomer for the production of polyester resins. Undoubtedly, the production of 1,2-PDO from glycerol will be a sustainable and feasible alternative to the current petroleum-based 1,2-PDO production method.

In general, the hydrogenolysis of glycerol is studied under heterogeneous conditions over various metal catalysts. Several recent reviews have summarized relevant catalytic systems for the glycerol hydrogenolysis reaction [1–3]. In order to obtain a good catalytic performance, metal catalysts are usually used in combination with a certain acid or base additive [2,3]. For example, H₂WO₄ [4], cation-exchange resin [5–7] and Nb₂O₅ [8] are effective acid additives, which can enhance the reaction rate and the diol selectivity over Ru or Rh catalysts. Regarding the base additives, Wang and Liu [9] and Maris et al. [10,11]

found that the addition of NaOH markedly increased the reactivity of Cu, Ru or Pt catalysts, but a certain amount of lactic acid was formed at high pH. In our previous works [12–16], we have developed a series of Ru-based catalysts, which exhibited good performances in the hydrogenolysis of glycerol to 1,2-PDO. Using LiOH as additive, both the conversion of glycerol and the selectivity to 1,2-PDO can be high up to 90% in the presence of Ru/TiO₂ catalyst [12–14]. We have also demonstrated that the base aids the initial dehydrogenation of glycerol to glyceraldehyde and promotes the dehydration of glyceraldehyde to 2-hydroxyacrolein (see Scheme 1) [12]. This effect of the base additive is responsible for the enhancement in the reaction rate and 1,2-PDO selectivity.

Although the introduction of some additives can promote the catalytic performance, it results in many troubles in practical manipulation, such as the product separation and catalyst recycling. According to the reaction pathway in Scheme 1, a catalyst that contains both metal sites and base sites should also achieve good results in the glycerol hydrogenolysis reaction. Solid-base supported metal catalysts will make it possible for the successful combination of metal sites and base sites. Such metal–base bifunctional catalysts bring the advantage that the product separation or catalyst recycling will be more maneuverable and more practicable. In fact, solid-base supported Pt catalysts [17] and Cu catalysts [18–21] are indeed efficient for the selective hydrogenolysis of glycerol to 1,2-PDO. As a typical example, the research group of Hou [18–20] developed a series of Cu-based catalysts supported on the

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Scheme 1. Hydrogenolysis of glycerol to 1,2-PDO over Ru-based catalyst in basic aqueous solution.

layered double hydroxalcalite-like compounds. These Cu-based catalysts were highly selective for 1,2-PDO. However, the catalyst preparation procedure seems a bit complicated and unmanageable.

In this work, we directly utilize the surface basicity of several easily available supports to modify the Ru catalyst, with the intent of developing a simple and additive-free catalytic system. Several Ru catalysts supported on basic oxides (CeO₂, La₂O₃ and MgO) were prepared and examined for the glycerol hydrogenolysis reaction. Ru/CeO₂ was found to be an efficient catalyst for the hydrogenolysis of glycerol in an additive-free aqueous solution.

2. Experimental

2.1. Catalyst preparation

Ru catalysts (Ru/CeO₂, Ru/La₂O₃ and Ru/MgO) with a metal loading of 3 wt.% were prepared by impregnation technique. Weighed amounts of the corresponding oxide were impregnated with the aqueous solution of RuCl₃. After impregnation, the solvent was removed, and the resulting powder was dried in vacuum at 110 °C for 10 h. All the catalysts were reduced in an autoclave by hydrogen at 200 °C. For more details, see the Supplementary material.

2.2. Characterizations

The Ru catalysts were characterized by ICP-AES, BET, XRD, XPS, and TEM. According to the references [22,23], the surface basicity features of the oxide supports were determined by the benzoic acid titration method using two Hammett indicators: bromothymol blue (pK_a = +7.2) and 2,4-dinitroaniline (pK_a = +15.0). The base strength (H₋) was expressed by the Hammett function that was scaled by the pK_a values of the indicators. The details are discussed in the Supplementary material.

2.3. Catalytic performance testing

Hydrogenolysis of glycerol was carried out in a 30 mL stainless steel autoclave. Because of the word count limit, more details are presented in the Supplementary material.

3. Results and discussion

3.1. Characterization of catalysts and supports

Some characterization results are shown comparatively in Table 1. ICP-AES results show that the Ru weight loadings are near to the stated value, i.e., about 3 wt.%. The BET surface area of Ru/MgO is the highest, while that of Ru/La₂O₃ and Ru/CeO₂ is very close. The Ru particle sizes are all determined by TEM due to weak diffraction peaks of Ru in the XRD patterns. Obviously, Ru particles are smaller on MgO and CeO₂

than those on La₂O₃. Our previous studies [13,14] have shown that the support material can significantly influence the metal particle size. The bigger Ru particles on La₂O₃ may be related to the fact that Ru particles are easier to agglomerate in this support.

As presented in Table 1, the Ru⁰/(Ru⁰ + Ru^{δ+}) refers to the surface Ru atomic ratios obtained from XPS experiments, where Ru⁰ represents the Ru atoms with metallic state and Ru^{δ+} represents the Ru species with intermediate value between Ru⁰ and Ru³⁺. The calculation method is referred to our earlier work [13]. It can be seen from Table 1 that the Ru species on Ru/La₂O₃ and Ru/CeO₂ are completely reduced in the reduction process. This indicates that the rare earth element is beneficial to the reduction of Ru, which is in agreement with the findings of Yu and co-workers [24]. A typical Ru 3d XPS spectrum of Ru/CeO₂ is shown in Fig. 1. The singlet in dotted line is attributed to C 1s (binding energy = 284.9 eV). This is an unavoidable contamination signal of the spectrometer [13]. There is only one doublet of Ru 3d (binding energy: Ru 3d_{5/2} = 280.1 eV, Ru 3d_{3/2} = 284.3 eV), which is assigned to the metallic ruthenium. For reference, the Ru 3d XPS spectra of Ru/MgO and Ru/La₂O₃ are shown in Figs. S1 and S2 (Supplementary material), respectively.

The XRD patterns of the supported Ru catalysts are illustrated in Fig. 2. The crystalline phases were identified by comparison with JCPDS files. For Ru/CeO₂, the clear diffraction peaks at 2θ = 28.6°, 33.1°, 47.5°, 56.4°, 59.1°, 69.4°, 76.7°, 79.1° and 88.4° are all attributed to cerianite CeO₂ (JCPDS Card #34-0394). In the case of Ru/MgO, the intensive and sharp diffraction peaks at 2θ = 18.6°, 32.8°, 38.0°, 50.8°, 58.6°, 62.1°, 68.2°, 72.0° and 81.2° can be assigned to brucite Mg(OH)₂ (JCPDS Card #83-0114), indicating that MgO is converted to Mg(OH)₂. This hydration of MgO mainly results from the hydrothermal condition used in the catalyst preparation process [25]. In the XRD pattern of Ru/La₂O₃, a new phase of La(OH)₃ (2θ = 15.7°, 27.4°, 31.6° and 48.4°; JCPDS Card #75-1900) is observed accompanied with the phase of La₂O₃ (2θ = 27.9°, 39.6° and 49.5°; JCPDS Card #89-4016). The existence of La(OH)₃ could be also owing to the hydrothermal condition in the catalyst preparation process [26]. Accordingly, CeO₂ is comparatively stable under the condition we used. As far as the Ru crystalline phase is concerned, no obvious diffraction peaks can be observed in the XRD patterns of Ru/CeO₂ and Ru/MgO, suggesting that the Ru particles on CeO₂ and MgO are too small to be detected. In contrast, the diffraction peaks of metallic Ru at 2θ = 38.4° and 42.2° (JCPDS Card #89-3942) appeared in the Ru/La₂O₃ catalyst. The particle size of Ru is determined

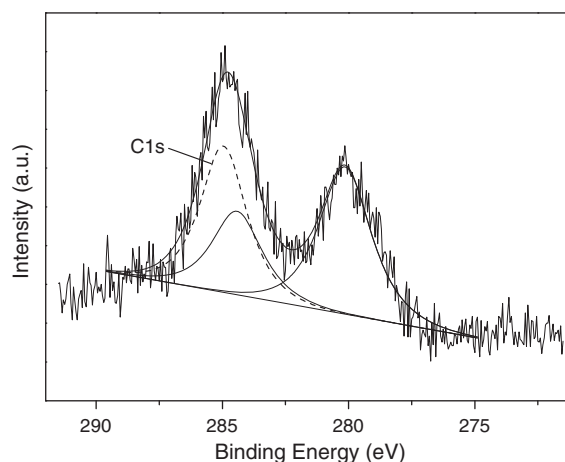


Fig. 1. Ru 3d XPS spectrum of Ru/CeO₂ catalyst.

Table 1

Some characterization results of the Ru catalysts.

Catalyst	Ru loading (wt.%)	BET surface area (m ² /g)	Ru particle size (nm) ^a	Ru ⁰ /(Ru ⁰ + Ru ^{δ+}) (%)
Ru/La ₂ O ₃	3.11	59	11.4	100
Ru/MgO	2.98	246	5.8	57.1
Ru/CeO ₂	3.03	63	5.3	100

^a Determined by TEM.

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