

Effect Of Solid Acids In The Conversion Of Glycerol Over Ru/Bentonite Catalyst In Glycerol Hydrogenolysis Reaction

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Abstract

Glycerol known as by-product of transesterification of vegetables oil become an important materials after some chemical modification. In this study, hydrogenolysis reaction of glycerol to 1,2-propanediol was conducted using various supported ruthenium based catalyst. The support materials used in this study are bentonite, TiO₂, Al₂O₃ and SiO₂. All experiments were carried out at reaction condition of 150°C, hydrogen pressure 20-30 bar for 7 hours and the 20%(wt) glycerol content in distilled water. The result shows that activity of the catalyts increased following this order: Ru/SiO₂ < Ru/TiO₂ ≈ Ru/Al₂O₃ < Ru/bentonite. High selectivity to 1,2-propanediol was obtained in hydrogenolysis glycerol over Ru/TiO₂ (83.7%) and Ru/bentonite (80.1%) catalysts. Since Ru/bentonite catalyst performed better than other tested catalyst, we choose this catalyst system to investigate the effect of various solid acids (zeolite, ZrO₂, Nb₂O₅ and amberlyst) on conversion of glycerol in hydrogenolysis reaction. Addition of solid acid in hydrogenolysis glycerol had promote the activity of Ru/bentonite catalyst drastically. The result shows that the presence of zeolite make the conversion of glycerol increased to maximum from 62.8% to 81.6% compared the other solid acids. Interestingly, selectivity to 1,2-propanediol still was achieved over 80.0%. These catalysts system were characterized by XRD, XPS, BET, and TEM for obtaining some physicochemical properties of the catalysts.

Keywords : solid acid; glycerol; hydrogenolysis; ruthenium catalyst; bentonite

1 INTRODUCTION

Transesterification of triglycerides with methanol in the presence of basic or acidic catalysts produced biodiesel that consists of fatty acid methyl esters. Every 9 kg of biodiesel production, about 1 kg of crude glycerol by-product is also formed [1]. Nowadays, biodiesel derived from vegetable oils and animal fats has received considerable attention. The recent rapid development of biodiesel processes has caused some concern over the oversupply of glycerol in the glycerol market. The glycerol market will likely to be saturated because of limited utilization of glycerol at the present time [2]. Recently, catalytic conversion of glycerol to other value product via hydrogenolysis reaction has received considerable attention.

The hydrogenolysis of glycerol produces 1,2-propanediol (1,2-PDO) and ethylene glycol (EG) as a major products with a 4% annual market growth [3]. Typical uses of 1,2-propanediol are in production of unsaturated polyester resins, functional fluids, pharmaceuticals, cosmetics, paints, etc [4]. Therefore, the new usages of glycerol are being requested widely. Several groups have reported on different catalyst systems, including supported transition metal catalyst such as Rh, Ni, Ru, Pt, Pt-Ru and Cu catalyst, for the hydrogenolysis of glycerol [5-13]. Previous study have been reported that among the metal catalysts, supported Ru catalyst was the most active for the hydrogenolysis of glycerol [14]. Previous research shows that hydrogenolysis of glycerol to propanediols proceed via dehydration of glycerol to acetol on acid catalysts and consecutive hydrogenation over metal catalysts. [15, 16]. Thus, a hydrogenolysis reaction is known as a bifunctional reaction. It requires catalysts both for dehydration and for hydrogenation functionality. According to the previous report, acid catalysts play an important role in hydrogenolysis reaction. Different solid acid catalysts such as zeolite, sulfated zirconia, tungstic acid and ion exchange resin have been studied as acid catalyst[17].

Best of our knowledge, there are a few reports using solid acid as co catalyst during glycerol hydrogenolysis over supported Ru catalyst, but there no study or report on Ru/bentonite catalyst system. Therefore, in the present study glycerol hydrogenolysis will carried out over Ru/bentonite using at different solid acid catalyst (zeolite, ZrO_2 , Nb_2O_5 and amberlyst) in order to investigate the effect of these solid acids on its conversion and selectivity.

2 EXPERIMENTAL

2.1 Catalyst preparation

Glycerol (99.9%), ruthenium trichloride, RuCl_3 were purchased from Sigma-Aldrich. The TiO_2 , bentonite, SiO_2 and Al_2O_3 used as support were obtained from Sigma-Aldrich also. The support materials were calcined in air at 500°C for 3 hours before used to remove moisture and impurities. All supported catalysts with 5% metal loading were prepared by impregnation method. The precursor used for Ru was RuCl_3 .

2.2 Catalyst characterization.

The surface area of the supported metal catalyst was measured using the Brunauer-Emmett-Teller (BET) method (N_2 adsorption) with a Gemini apparatus (Micromeritics 2010 Instrument Corporation). Transmission Electron Microscope (TEM) images were taken for determination of the particle size with a CM12 instrument (Philips) operated at 200 kV. The samples were dispersed by supersonic waves in ethanol. Then they were placed on Cu grids under air atmosphere. General morphology information of the samples were examined by Field Emission Scanning Electron Microscope (FESEM) with LEO 1450VP model equipped with energy dispersive X-ray detector (EDX). All the samples were analysed in a high-vacuum mode at 20 kV. The phase structures of the catalysts were determined by X-Ray Diffraction (XRD) patterns using Bruker AXS D8 Advance X-ray Powder Diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.15406 \text{ nm}$) at angle $2\theta = 20 - 80$. About 2.0 gram of sample was grinded and the fine powder was pressed on the holder of diffractometer. The X-ray photoelectron spectrum (XPS) data of the as-prepared samples were obtained with an XPS type ultra from kratos. Sample was analysed at 3×10^{-9} Torr. The binding energies were referenced to the C 1s line at 284.5 eV from adventitious carbon. This C 1s at 284.5 eV was used to calculate the different binding energy (ΔBE) between C 1s peak in the samples.

2.3 Catalytic reaction and product analysis.

The catalytic hydrogenolysis reactions were carried out in a 50 ml stainless-steel with teflon liner autoclave, PARR reactor equipped with an electronic temperature controller and a mechanical stirrer. Reaction was normally conducted under the following standard conditions : 150°C temperature, 20 bar initial hydrogen pressure, 1.0 g catalyst weight, 23 ml of 20 wt% aqueous solution of glycerol, 7 h reaction time and at constant stirring speed at 200 rpm.

The hydrogenolysis reaction sequence was as follows: loading of the reactor with aqueous solution of glycerol and the appropriate amount of catalyst. Then the reactor was flushed three times with N₂ in order to remove oxygen gas and pressurized with H₂ to 20 bar. The mixture of glycerol and the catalyst was heated up to 150°C at constant stirring speed at 200 rpm and maintained for 7 hours.

After the reaction, the reactor was cooled at room temperature and the liquid phase products were separated from the catalyst by centrifuge at 4000 rpm during 15 min then filtered. These products were analysed using a gas chromatograph (GC-Hewlett Packard Model 6890N) equipped with a flame ionization detector (FID). The gas chromatograph (GC) column used was a DB-WAX capillary column (30 m x 0.32 mm x 0.5 µm) manufactured by Angilent Technologies. Solutions of n-butanol and 1,4-butanediol with known amounts of internal standards were used for quantification of various glycerol-derived compounds in the product.

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

The physico-chemical properties of the support material and 5%(wt) supported Ru catalysts used in this study are shown in Table 1. The BET specific surface area of support TiO₂, bentonite, SiO₂ and Al₂O₃ were found to be 8.8 m²g⁻¹, 101.3 m²g⁻¹, 130.5 m²g⁻¹ and 155.6 m²g⁻¹ respectively. Analysis BET showed that support material namely bentonite, SiO₂ and Al₂O₃ have similar BET surface area value in the range (100-150) m²/g except TiO₂ has the lowest BET surface area value.

Table 1 : Surface area of supports and supported catalyst

Support	BET Surface Area, m ² /g	Supported Catalysts	BET surface area (m ² /g)
Bentonite	101.3	Ru/bentonite	35.4
TiO ₂	8.8	Ru/TiO ₂	7.9
SiO ₂	130.5	Ru/SiO ₂	125.3
Al ₂ O ₃	155.6	Ru/Al ₂ O ₃	141.4

BET surface area of Ru/bentonite, Ru/TiO₂, Ru/SiO₂ and Ru/Al₂O₃ catalysts obtained are 35.4, 7.9, 125.3 and 141.4 m²/g respectively. BET analysis revealed that catalyst of Ru/SiO₂ and

Ru/Al₂O₃ have similar surface area, meanwhile Ru/TiO₂ has the smaller surface area. Previous study have claimed that the decrease in BET surface area value of the catalysts after 5% (wt) Ru loading is due to pore blockage of support by crystallites of Ru [14].

The series of these catalysts were characterized by XRD as shown in Fig.1. As we can see, Ru supported on TiO₂ have crystalline form whereas Ru supported on Al₂O₃, bentonite and SiO₂ have amorphous phase. It seem that XRD pattern of Ru/bentonite shows weak diffraction peak at $2\theta = 40.5^\circ$, 43.0° and 55.0° which could be assigned to RuO₂ species. On the other hand, there are no characteristic peak related to metallic Ru was observed for Ru/AlO₃, Ru/SiO₂ and Ru/TiO₂. Previous study shows that the absence of peak Ru particles at low content (5% metal loading) might be due to the presence of nano Ru particles in a highly dispersed on the supports [18].

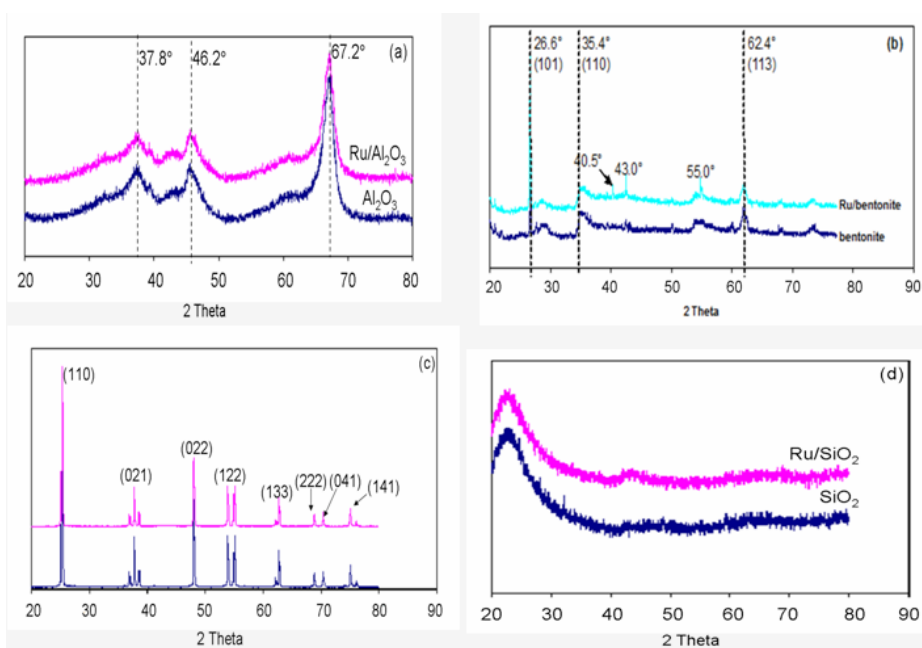


Figure 1 : XRD pattern of Al₂O₃ and 5%(wt) Ru/AlO₃(a), bentonite and 5%(wt) Ru/bentonite(b), TiO₂ and 5%(wt) Ru/TiO₂ (c), SiO₂ and 5%(wt) Ru/SiO₂

Since XRD pattern did not shows the peak related to Ru particle, therefore in order to study the existence of Ru element on the support, XPS analysis was done. Fig. 2 illustrate the XPS

wide scan spectra of Ru/Al₂O₃(a), Ru/Bentonite(b), Ru/TiO₂(c), Ru/SiO₂(d). As we can see, wide scan spectra clearly shows the presence of Ru species on the supports. The presence of Ru species cause peak of Ru_{3d} appear in the XPS spectra of each catalyst.

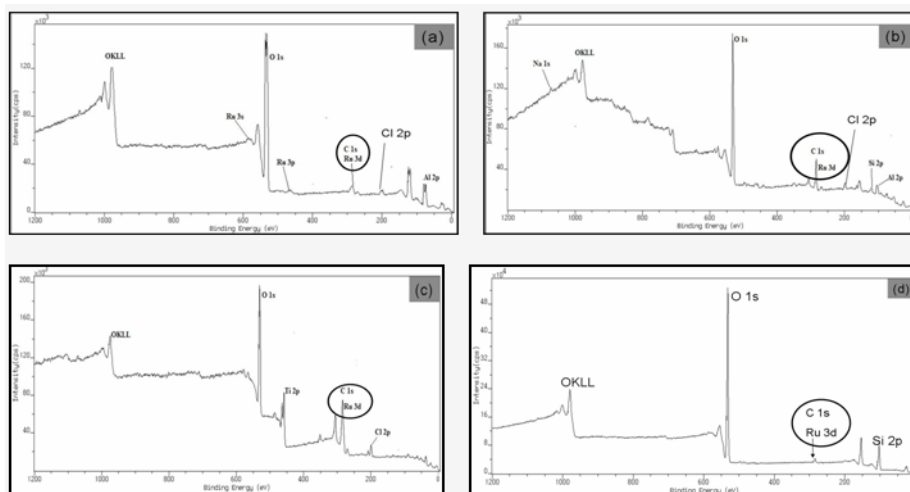


Figure 2 : XPS spectra wide scan spectrum of Ru/Al₂O₃(a), Ru/Bentonite(b), Ru/TiO₂(c), Ru/SiO₂(d)

Chemical state of the Ru element was investigated via narrow scan and the spectra are shown in Fig.3. Since the binding energy (B.E) of Ru 3d_{5/2} (280 eV) overlapped with that C 1s (284.5 eV), it was difficult to resolve the small Ru peak out from the large peak of C 1s. The Ru 3d spectra revealed the presence of two different chemical states on the surface (Ru⁰ at 281.0 eV and Ru⁴⁺ at 283.3 eV) except Ru species on bentonite shows chemical state of Ru⁰ species only. Previous study have found that B.E of ≈ 283.0 eV was assigned to RuO₂ which is corresponding to Ru⁴⁺ species.[14] Meanwhile according to Balaraju et al. the B.E value of Ru⁰ species was in the range 280-281 eV.[14] The presence of Ru⁴⁺ species indicated the Ru exists as oxide form and this species might be formed during calcinations process.

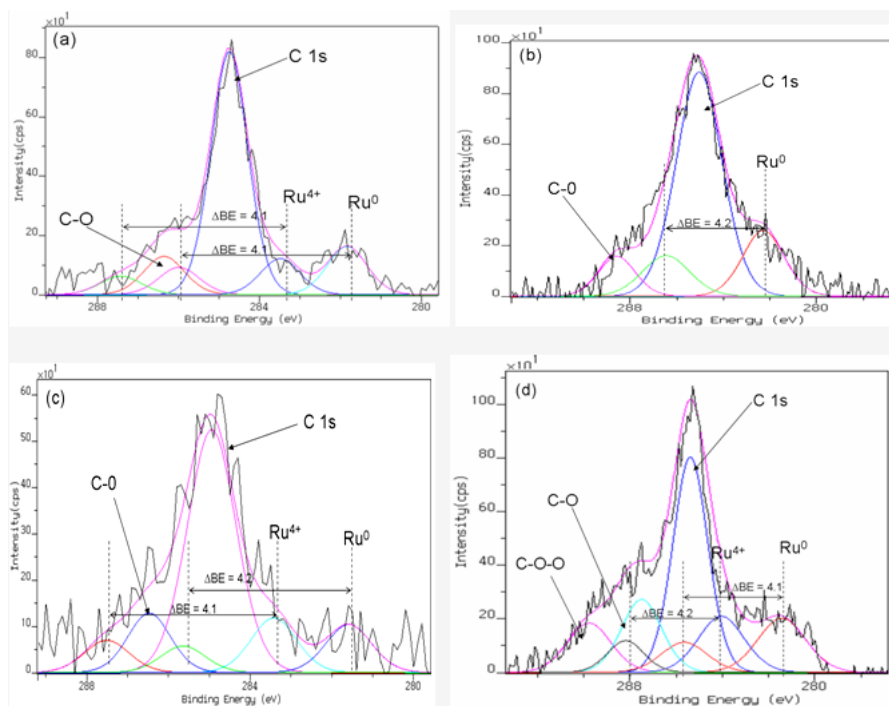


Figure 3 : XPS spectra of narrow scan of the Ru region for Ru/Al₂O₃(a) , Ru/bentonite (b), Ru/TiO₂(c) and Ru/SiO₂(d)

FESEM-EDX analysis was done to investigate further the dispersion of Ru particles and it seems that Ru particle is more dispersed on bentonite support and this result was related with catalytic activity of Ru catalyst. Fig. 4 illustrated the morphology of the catalyst analyze by TEM and the average size particle measured by TEM of Ru particle on bentonite, Al₂O₃, SiO₂ and TiO₂ were ≈ 1.5 nm, < 2 nm, ≈ 2 nm and 4-6 nm. This result indicate that size particles of Ru were much smaller on bentonite support than others support.

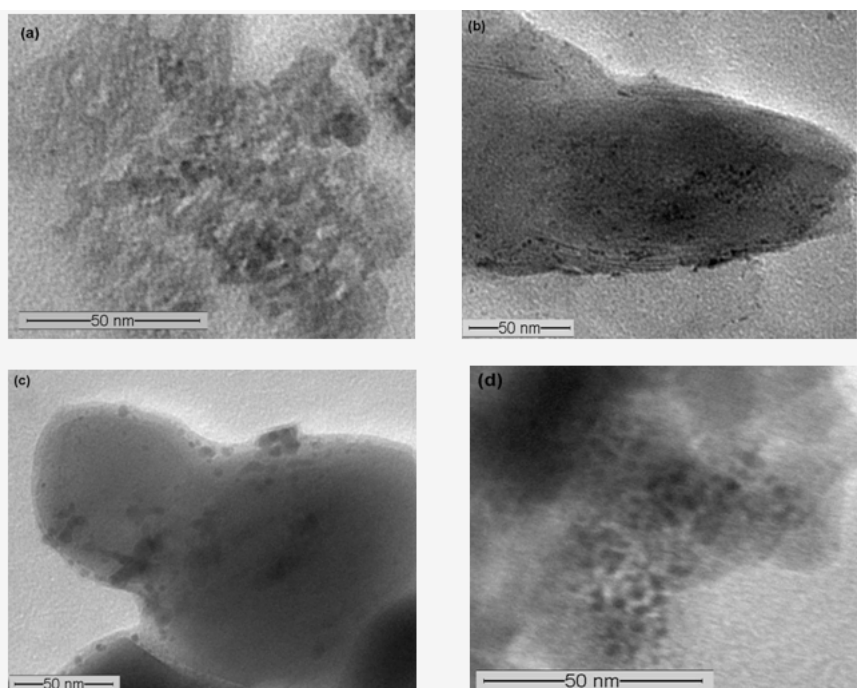


Figure 4 : TEM image of Ru/Al₂O₃(a), Ru/Bentonite(b), Ru/TiO₂(c), Ru/SiO₂(d)

3.2 Hydrogenolysis glycerol

The effect of support materials on catalytic behavior of Ru catalyst for hydrogenolysis glycerol was investigated under mild reaction condition of 150°C, 20 bar initial hydrogen pressure for 7 hours reaction time. The concentration of glycerol in distilled water was 20%(wt). Table 1 summarized the activities of glycerol hydrogenolysis over Ru metal catalyst supported on bentonite, TiO₂, Al₂O₃ and SiO₂. The result shows that Ru/bentonite exhibited the most active (62.8%) in hydrogenolysis glycerol meanwhile Ru/TiO₂ gave the highest selectivity (84.4%) to 1,2-propanediol. The result also revealed that all the catalysts gave same selectivity to EG.

From the results, it is clear that these catalysts were favour to C-O breaking bond compared to C-C bond. Therefore, product 1,2-propanediol considered as a main product in hydrogenolysis glycerol using this system catalyst. The activity of the catalyst was not related with high surface area, since Ru/bentonite catalyst did not possess the highest surface area. The BET surface area value

following this: $\text{Ru/Al}_2\text{O}_3 > \text{Ru/SiO}_2 > \text{Ru/bentonite} > \text{Ru/TiO}_2$. This result also implies that glycerol conversion greatly depend on the nature of the support. Previous study was found that solid base (hydrotalcite and MgO) supported Pt catalysts exhibited the predominant activity and higher 1,2-propanediol selectivity than of solid acids (Al_2O_3 , H-ZSM5 and H-Beta) [19]. In our case, bentonite which is base material support shows better catalytic performance and this result was quite similar with previous report.

Table 1: Glycerol hydrogenolysis over supported Ru catalysts.

Catalyst	Glycerol conversion(%)	Selectivity (%)	
		1,2-PDO	EG
Ru/bentonite	62.8	80.1	9.9
Ru/TiO ₂	38.8	84.4	11.2
Ru/Al ₂ O ₃	38.9	71.0	12.7
Ru/SiO ₂	15.6	76.3	7.0

Reaction conditions: 20 (wt%) glycerol in water, H₂ pressure = 20-30 bars, reaction time = 7 hrs

Since Ru/bentonite catalyst performed better among the tested catalyst, so we choose this catalyst for further investigation. Different solid acid catalyst as co-catalyst are added in Ru/bentonite catalyst during glycerol hydrogenolysis reaction and the results are shown in Table 2. It was found that activity of Ru/bentonite increased when using solid acid as the additive/co-catalyst. The order of activity for the solid acid catalysts are as follow: zeolite > ZrO₂ > Nb₂O₅ > Amberlyst. The result revealed that the highest activity of the catalyst obtained when zeolite was used as solid acid. Interestingly the selectivity towards 1,2-propanediol was also high. Previous studied have reported that activity of the catalyst was high when Amberlyst is used as the solid acid catalyst and they also found that Amberlyst decomposes under reaction condition more than 120°C [17]. Similar result was obtained in this study since activity of the Amberlyst catalyst exhibited the lowest activity.

Table 2 : Influence of solid acid as co-catalyst in the hydrogenolysis of glycerol reaction over Ru/Bentonite catalyst

Metal catalyst	Acid catalyst	Conversion(%)	Selectivity (%)	
			1,2-PD	EG
Ru/bentonite	-	62.8	80.1	9.9
Ru/bentonite	zeolite	81.6	81.5	8.5
Ru/bentonite	ZrO ₂	77.6	77.7	10.0
Ru/bentonite	Nb ₂ O ₅	75.5	83.6	11.4
Ru/bentonite	Amberlyst	69.4	8.0	-

Reaction conditions: 20 (wt%) glycerol in water, H₂ pressure = 20-30 bars, reaction time = 7 hrs

4 CONCLUSIONS

The solid acid as a co-catalyst influences the conversion of glycerol during hydrogenolysis over Ru/bentonite. This study indicates that the catalyst activity greatly depends on the types of solid acid used during the hydrogenolysis reaction. Among different solid acid catalysts studied, zeolite exhibited better activity. Further research has to be carried out in order to study the amount of acid site and the synergistic effect towards glycerol conversion and selectivity to 1,2-propanediol.

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