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EFFECT OF RUTHENIUM METAL PRECURSOR SUPPORTED ON BENTONITE FOR HYDROGENOLYSIS GLYCEROL

[1,2]**Noraini Hamzah**, [2]Aznira Alias, [2]Mohamad Kassim, [2]Mohd Ambar Yarmo*

***Abstract*—**Various ruthenium precursor (Ru= $RuCl_3$, Ru2 = $Ru(acac)_3$, Ru3 = $Ru_3(CO)_{12}$) supported on bentonite were prepared by conventional impregnation method. Their catalytic performances were evaluated in the hydrogenolysis of glycerol using autoclave Parr reactor under mild reaction conditions of 150°C, hydrogen pressure 30 bar for 7 hours. Among the studied catalyst, 5% Ru/bentonite catalyst prepared form Ru and Ru3 precursor exhibited higher and similar activity which are (79.6%) and 72.5% respectively. In contrast, Ru2/bentonite prepared from $Ru(acac)_3$ precusor gave lowest activity (41.8%). In term of selectivity to 1,2-propanediol, Ru2 and Ru3 precusor gave higher and similar selectivity (67% and 66.9%) compared to Ru precursor (50.6%). These results indicated that metal precursor plays the important role on activity and selectivity of the catalyst. The catalysts were characterized by XRD, XPS, BET, FESEM-EDX and TEM, and the reasons for the high performances of the catalyst were also discussed.

Keywords:Glycerol,Hydrogenolysis,Nano-ruthenium, Propanediol, Bentonite

Noraini Hamzah is in School of Chemical Sciences and Environmental ,Faculty of Applied Sciences ,University of Technology MARA 40450, Shah Alam, Malaysia(phone: 012 6798930; fax :03-03-89215410; (e-mail:norainihamzah@gmail.com)
Aznira Alias is with School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia ,43600 Bangi, Selangor Darul Ehsan, Malaysia (e-mail:azniraalias@yahoo.com)
Mohd Ambar Yarmo is in *School of Chemical Sciences and Food Technology,Faculty of Science and Technology, Universiti Kebangsaan Malaysia ,43600 Bangi, Selangor Darul Ehsan, Malaysia (e-mail: ambar@ukm.my)*
Mohamad Kassim is in *School of Chemical Sciences and Food Technology,Faculty of Science and Technology, Universiti Kebangsaan Malaysia ,43600 Bangi, Selangor Darul Ehsan, Malaysia (e-mail:mbkassim@ukm.my)*

I. INTRODUCTION

Catalytic conversion of renewable biomass resources, as feedstocks for the chemical industry, becomes more and more important because of the worldwide and seroius energy and environment problems [1]. Transesterification of triglycerides with methanol in the presence of basic or acidic catalysts produced biodiesel that consists of fatty acid methyl esters (Figure 1). Production of every 9 kg biodiesel, about 1 kg of crude glyderol by-product is also formed [2].

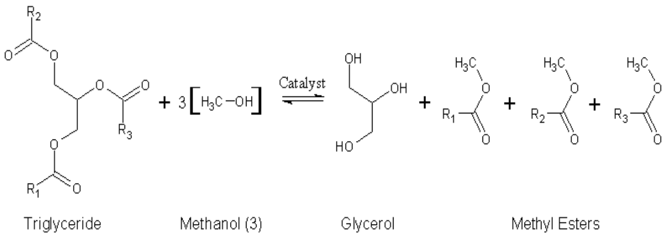


Figure 1 : Transesterification of triglycerides with methanol

Nowadays, biodiesel derived from vegetable oils and animal fats has received considerable attention. The recent rapid development of biodisel 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 [3]. It is known that glycerol can be catalytically converted into functionalized and value-added chemical via a variety of reaction routes such as oxidation, hydrogenolysis, dehydration, pyrolysis, steam reforming, etherification, esterification, oligomerization and polymerization [4]. 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 [5]. Typical uses of 1,2-propanediol are in unsaturated polyester resins, functional fluids, pharmaceuticals, cosmetics, paints, etc [6]. Finding new outlets for glycerol consisting of high value-added products would improve the economy of the whole process and could potentially offer great environment benefits.

Conversion of glycerol using supported catalyst has been extensively studied by several groups [1-3], [5-7],[8-12]. For example, [10] prepared supported Cu catalyst on γ-Al_2O_3 and found that this catalyst could maintain its high selectivity (about 95%) compared with a commercial copper chromite catalyst under the same conditions. [5] investigated the combination of Rh/C and H_2WO_4 was effective for the hydrogenolysis of glycerol to 1,3 propanediol at low conversion level. Others studies by [7] found that addition of solid acid (Nb_2O_5) as co-catalyst influences the conversion of glycerol during its hydrogenolysis over Ru/C catalyt. More recently, [12] reported that 5 wt% Ni/SiO_2 catalyst give 30% glycerol conversion with 98% selectivity to propylene glycol at 200°C reaction temperature, 20-25 bar hydrogen pressure for 8 hours.

Most of the researcher interesting to improve conversion and selectivities by focusing on metal types, reaction temperature, hydrogen pressure and catalyst loading(Jian Feng et al. 2008). However, there are little paper reported on the catalytic performance of hydrogenolysis glycerol based on the effect of metal precusor. Studies by [3] found that the support material can influence the Ru metal particle size of the catalyst, and the hydrogenolsis of glycerol is more active on small metal particles.

Therefore, this study deals with the effect of metal precusor on bentonite as support material on catalytic performance of ruthenium(Ru) catalysts in the hydrogenolysis glycerol. The scope of this study was to evaluate the effect of metal precursor on the structure and physicochemical characteristics of the catalyst as well as the performance in the glycerol hydrogenolysis reaction. In addition, the use of three different ruthenium precusors ($RuCl_3$, $Ru(acac)_3$ and $Ru_3(CO)_{12}$) for the preparation of the catalyst and their effect on the properties and catalytic performance of the Ru supported catalysts was investigated.

II. EXPERIMENTAL

Catalyst preparation

All supported ruthenium catalysts were prepared by impregnation method. The clay mineral used in this work is a calcium-rich bentonite (CaB) was obtained as powder from PT Superintending Company of Indonesia also used as support. The bulk chemicak analysis of bentonite(mass%) is SiO_2, 64.15; TiO_2, 0.47; CrO_3, 0.003; Al_2O_3, 0.70; Fe_2O_3, 0.10; MgO, 0.70; CaO, 0.03; Na_2O, 0.20; K_2O. 0.50 and loss on ignition (LOI), 22.61. Bentonite supports was calcined in air at 500°C for 3 hours before used to remove moisture and impurities. Ruthenium was loaded on the support using three different precusors : ruthenium acetylacetonate, $Ru(acac)_3$, triruthenium dodecarbonyl, $Ru_3(CO)_{12}$ and ruthenium chloride, $RuCl_3$. The metal loading of ruthenium metal is 5% and it was kept the same. For preparation with a nominal metal loading of 5 wt%, 100 mg of Ru-based catalyst was dissolved in acetone and stirred at room temperature for a few minutes. This resulting solutions was poured into the support (1800 mg) and sonicate for 60 min. Similar procedures were used for the other precusors. The catalysts were then dried in oven at 60°C during 12 h and further reduced with a hydrogen stream at 100°C for 60 min. Then the catalyst were used directly for hydrogenolysis without any further treatment.

Catalyst characterization

The phase structures of the catalysts were determined by X-Ray Diffraction (XRD) patterns with Bruker D8 Advance X-ray Powder Diffractometer with Cu Kα (λ= 0.15 nm) at angle 2θ. The X-ray photoelectron spectrum (XPS) data of the as-prepared samples were obtained with an ESALab220i-XL electron spectrometer from VG Scientific using 300 W Mg$K\alpha$ radiation. The base pressure was abaout 3 x 10^{-9} mbar. The binding energies were referenced fo the C 1s line at 284.5 eV from adventitious carbon. Transmission electron microscope (TEM) images were taken for determination of the particle size with a CM12 instrument (Philips) operated at 200 kV. General morphology information of the samples were examined by FESEM with LEO 1450VP model equipped with energy dispersive X-ray detector (EDX). All the samples were scanning in a high-vacuum mode at 20 kV. The surface area of the supported metal catalyst was measured using the BET method (N_2 adsorption) with a Gemini apparatus (Micromeritics Instrument Corporation).

Catalytic activity measurement

The catalytic hydrogenolysis reactions were carried out in a 50 ml stainless-steel 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 striring speed.

The hydrogenolysis reaction sequence was as follows: loading of the reactor with aqueous solution of glycerol and the approriate amount of catalyst. Then the reactor was flushed three times with N_2 in order to remove oxygen gas and pressurized with H_2 to 20 bar. The mixture of glycerol and the catalyst was heated up to 150°C at constant stiring speed 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 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.

The conversion of glycerol, the selectivity of propanediols , ethylene glycerol and other products (propanol (1,2) , ethanol and methanol) were the factors used to evaluate the catalyst performance. The conversion and selectiviy of glycerol are calculated as the following equations:

$$\text{Conversion (\%)} = \frac{\text{amount of glycerol converted (gram)}}{\text{Total amounts of glycerol in the feed (gram)}} \times 100\%$$

$$\text{Selectivity(\%)} = \frac{\text{amount of product produced (gram)}}{\text{amount of glycerol converted (gram)}} \times 100\%$$

Only selectivities to 1,2-propandieol (1,2-PDO) and ethylene glycol (EG) were discussed in this study in view of their commercial important and relative large amounts detected in the products.

III. RESULTS AND DISCUSSION

Catalyst characterization

The XRD patterns of the samples with different precusor of ruthenium catalysts supported on bentonite was shown in Figure 2. In the XRD profile, it seem that these catalysts were amorphous phase, however very weak diffraction peak might be RuO_2 species appear at different theta for different types of precusors. The small peak appear at 2θ = 45.8° and 2θ = 36.6° for $RuCl_3$ and precusor $Ru_3(CO)_{12}$ respectively. There are two small peak appears for Ru_3(acac) precusor at 2θ = 25.8° and 55.1°.

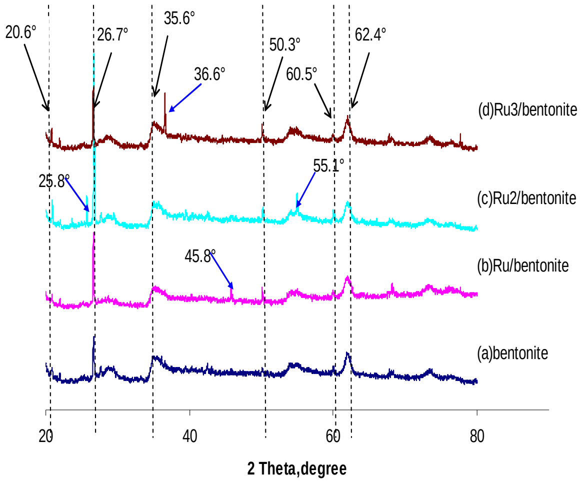


Figure 2 : XRD patterns of all precusors supported on bentonite

In order to investigate further the existence of Ru particle on the support XPS analysis was done. Figure 3 showed the XPS spectra wide scan of bentonite(a), Ru/bentonite(b), Ru2/bentonite(c) and Ru3/bentonite(d). As we can seen, pattern of the spectra was almost the same between Ru metal precursor and peak of Ru 3d can be observed with binding energy(BE) 281.0 eV. According to handbook of x-ray photoelectron spectroscopy [15], BE of $Ru_{3d5/2}$ was (280.1-285.0) eV. In contrast, there are small peak appear at the same binding energy with Ru 3d for bentonite wide scan. Some difficulties analyze in detail of peak Ru 3d was due to overlapping with peak C 1s region (284.5 eV). Therefore we can not analyze the narrow scan of Ru 3d peak in order to study the detail chemical state of Ru element in the catalyst.

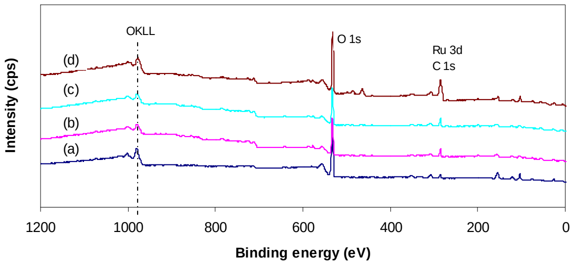


Figure 3 : XPS spectra wide scan of bentonite(a), Ru/bentonite(b), Ru2/bentonite(c), Ru3/bentonite(d)

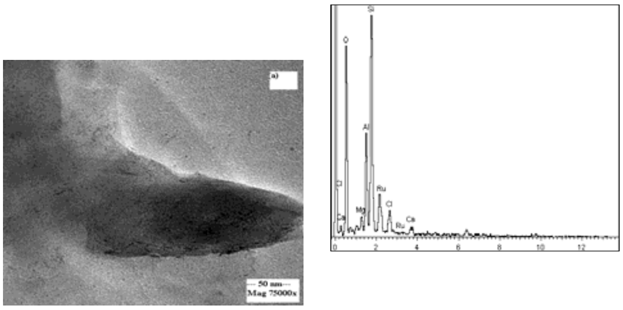
The physicochemical characteristics of the Ru-based supported catalysts were analyzed by BET and summarized in Table 1. It seem that surface area, S_A and external surface area were decreased when Ru metal was loaded into the support. This result indicate that Ru metal was successfully supported on the bentonite.

Table 1 Physicochemical catalyst characterization

Catalyst	Surface Area, S_A (m^2/g)	External Surface Area (m^2/g)	Micropore Area (m^2/g)	Micropore volume (m^2/g)
Bentonite	72.2	46.3	25.9	0.0133
Ru/bentonite	10.4	8.7	1.6	0.0008
Ru2/bentonite	6.8	1.9	4.7	0.0028
Ru3/bentonite	39.7	29.3	10.3	0.0053

Ru = $RuCl_3$, Ru2 = $Ru(acac)_3$, Ru3 = $Ru_3(CO)_{12}$,

Analysis TEM of all the catalysts were done in order to observe the microstructure image and particle size of prepared catalysts. Figure 4 illustrates the TEM images obtained for Ru/bentonite, Ru2/bentonite and Ru3/bentonite. The morphology and the microstructure of these catalysts were not much different for all precusors. Based on the TEM analysis, the average particles size of Ru on bentonite supports were 2-5 nm. This result revealed type of precursor not affected on the size of Ru particle. The shapes of ruthenium particles were approximately spherical particles and the boundary of ruthenium particles could be clearly observed. FESEM-EDX analysis (the micrographs of which are not shown for brevity) shows that Ru particle well dispersed on bentonite.



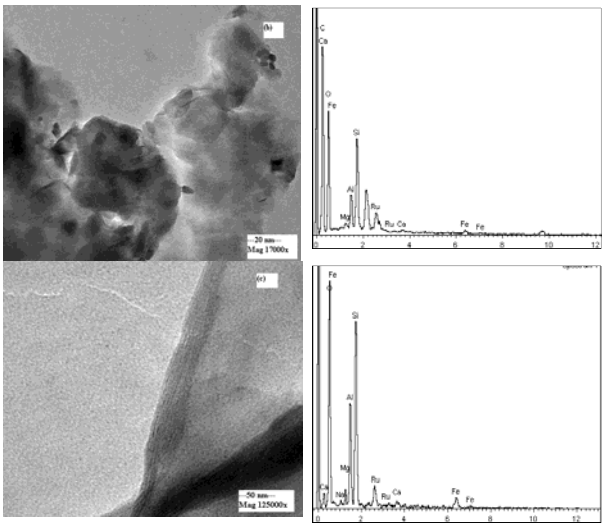
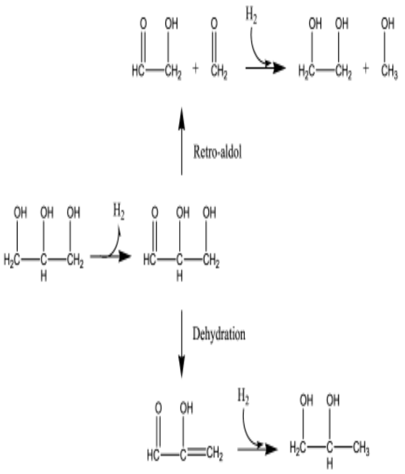


Figure 4: TEM images and EDX analysis of Ru/bentonite(a), Ru2/bentonite(b), Ru3/bentonite (c),

Hydrogenolysis of Glycerol

In our previous study, the optimum reaction temperature and time of reaction in the hydrogenolysis of glycerol over Ru-based catalyst has been already examined. Therefore, 150°C and 7 hours were chosen as the standard reaction conditions in present study. In order to maintain the reaction under mild condition, we decided to kept the pressure of hydrogen at 20-30 bar throughout the reaction.

Table 1 summarized the results of performances ruthenium based catalyst with different precusor (Ru, Ru2 and Ru3) supported on bentonite in the reaction of glycerol. The results clearly showed that the main reaction product of glycerol hydrogenolysis over supported Ru-based catalyst is 1,2-PDO and EG meanwhile product produced in minor amounts are 1-propanol, 2-propanol and methanol. Mechanism proposed by [14] suggested that the hydrogenolysis reaction is suggested to proceed via two route which are dehyration and retro-aldol (scheme 1). In retro-aldol route, involving C-C bond cleavage to form ethylene glycol and methanol. On the other hand, 1,2-propanediol is produced via C-O bond cleavage in dehyration route.



Scheme 1: Mechanism proposed by [14]

Table 1 : Catalytic performance of Ru-based catalyst on bentonite support in glycerol hydrogenolysis.

Catalyst	Support	Conversion	Selectivity of each product (%)				
		%	1,2-PDO	EG	ACETOL	PROPANOL(1-,2-)	MEOH
Ru	bentonite	79.9	50.6	12.4	6.5	2.9	-
Ru2	bentonite	41.8	67.1	8.7	-	0.8	-
Ru3	bentonite	72.5	66.9	27.5	0.9	-	0.6

Reaction conditions : 20-30 bar , 150°C, 1.0 g catalyst, 20 g of 20%(wt) glycerol, 7h.
(Ru = $RuCl_3$, Ru2 = $Ru(acac)_3$, Ru3 = $Ru_3(CO)_{12}$,)

Effect of Ru metal precursor

In this study, the effect of the Ru metal precusor on the performance of the catalyst using bentonite as support material was examined. As mentioned earlier, we using three types of Ru metal precusor (Ru =$RuCl_3$; Ru2= $Ru_3(acac)$; Ru3= $Ru_3(CO)_{12}$) which were loaded on the bentonite. Figure 5 presents conversion and product selectivities for studied catalyst evaluated in the glycerol hydrogenolysis reaction at 150°C and 30 bar H_2 pressure for 7 h reation time. As shown from the results, performance of supported Ru catalyst on bentonite support mainly affected by the different Ru metal precusor.

In term of conversion, we can see that bentonite supported prepared with Ru and Ru3 metal precusor are the most active with activity 79.6% and 72.5% respectively. When comparing catalyst of Ru/bentonite and Ru3/bentonite, activity of Ru/bentonite is slightly higher compared to Ru3/bentonite due to high percentage weight of Ru metal precusor on bentonite compared to other precusors. (Table 2). In contrast, Ru2 metal precusor showed less activity(41.8%). Meanwhile Ru2 and Ru3 metal precusor gave higher and similar selectivity(67% and 66.9%) to 1,2-PDO. On the other hand, Ru metal precusor gave slightly lower selectivity(50.6%) to 1,2 –propanediol.

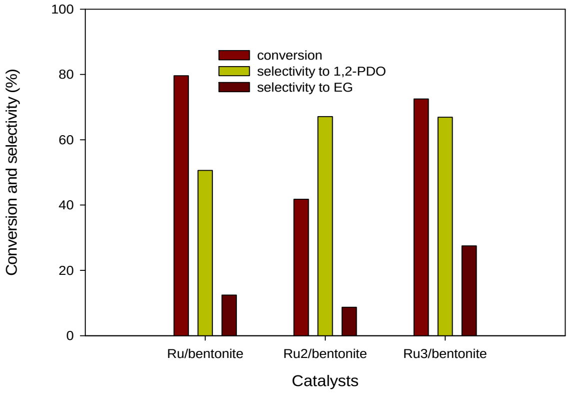


Figure 5 : Performance of Ru-based catalyst prepared with different precursor on bentonite. Ru = $RuCl_3$, Ru2 = $Ru(acac)_3$, Ru3 = $Ru_3(CO)_{12}$,

Our result is not similar with previous study by Vasiliadou et al. [2]. From literature [2], selectivity to 1,2-propanediol increased due to the presence of residual chloride ion (Cl^-).They claimed that the presence of Cl^- cause acidity of the catalyst increased. In term of selectivity to EG, Ru3 precusor gave almost double(27.5%) compared to Ru and Ru2. It seem that Ru3 precusor often promotes excessive C-C cleavage.

Table 2 : Percentange Ru metal on the support analysed by FESEM-EDX

Catalyst	Precusor	Support	% Ru metal
Ru	$RuCl_3$	bentonite	3.62
Ru2	$Ru(acac)_3$	bentonite	0.58
Ru3	$Ru_3(CO)_{12}$	bentonite	2.43

This study showed that Ru3 metal precusor supported on bentonite is the best catalyst for hydrogenolysis glycerol due to higher conversion(72.5%) and selectivity to 1,2-propanediol(66.9%) and ethylene glycol(27.5%) under mild condition .

IV. CONCLUSION

The results of this study indicate that types of Ru metal precusor significantly effect the performance and selectivity of product in glycerol hydrogenolysis. This study also revealed that bentonite which is cheap potentially a good as catalyst support material.

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REFERENCES

[1] H. Zhiwei, C. Fang, K. Haixiao, C. Jing. Characterization and catalytic properties of the CuO/SiO_2 catalysts prepared by precipitation –gel method in the hydrogenolysis of glycerol to 1,2-propanediol: Effect of residual sodium. *Applied Catalysis A*, 2009

[2] E.S. Vasiliadou, E. Heracleous, I.A. Vasalos, A.A Lemonidou. Ru-based catalyst for glycerol hydrogenolysis- Effect of support and metal precusor. *Applied Catalysis B:Environment* vol.92, pp 90-99. 2009

[3] F. Jian, F. Haiyan, W. Jinbo, L. Ruixiang, C. Hua, L Xianjun. Hydrogenolysis of glycerol to glycol over ruthenium catalyst: Effect of support and catalyst reduction temperature. *Catalysis Communation* vol. 9 , pp 1458-1464, 2007

[4] J. Tao, Z. Yinxi, L. Shuguang, L. Huizhen and H. Buxing. Hydrogenolysis of glycerol catalyzed by Ru-Cu bimetallic catalysts supported on clay with the aid of ionic liquids. *Green Chemistry*, vol. 11, 2009, pp 1000-1006.

[5] C. Julien, D. Laurent, G. Pierre, M. Philippe, P. Catherine and R. Cecille. Glycerol hydrogenolysis on heterogenous catalyst. *Green Chemistry*, vol. 6, pp 359-361, 2004

[6] P. Erin, J. D. Robert. Hydrogenolysis of glycerol over carbon-supported Ru and pt catalysts. *J of Catalysis*, vol. 249, pp 328-337, 2007

[7] M. Balaraju, V. Rekha, P.S. Sai Prasad, B.L.A Prabhavanthi Deva, R.B.N Prasad, N. Lingaiah. Influence of solid acids as co-catalysts on glycerol hydrogenolysis to propylene glycol over Ru/C catalysts. *Applied Catalysis A: General*, 2008, pp 82-87

[8] M. Lan, H. Dehua. Hydrogenolysis of glycerol to propanediols over higly active Ru-Re bimetallic catalyst. *Top Catalysis*. vol. 52, pp 834-844, 2009

[9] M. Tomohisa, K. Yohei, K. Kimio, T. Keiichi. Glycerol conversion in the aqueous solution under hydrogen over Ru/C + an ion-exchange resin and its reaction mechanism. *J of Catalysis*. 2006, 240, pp 213-221.

[10] G. Liyuan , M. Jingbo , G. Xinwen ,Z. Shuquang . Supported Cu catalysts for selective hydrogenolysis of glyycerol to propanediols. *Applied Catalyst A:General* : pp 93-98, 2009

[11] H. Long, Z. Yulei, Z. Hongyan, D. Guaqiang, L. Yongwang. Direct of conversion into 1,3-propanediol over $Cu-H_4SiW_{12}O_{40}/SiO_2$ in vapor phase. *Catalysis Letter*. vol. 131, pp 312-320, 2009

[12] M. Adriana, I. Gheorghe, G. Costinela-laura, C. Claudia, O. Spiridon. Glycerol hyrogenolysis to propylene glycol. *Catalysis Letter*. vol. 97, pp 315-320, 2009

13] M.A Dasari, P.P Kiatsimkul, W.R Sutterlin , G.J Suppes. Low-pressure hydrogenolysis of glycerol to propylene glycol. *Applied Catalyst A* 2005 vol. 281: pp 225-231

[14] T.Miyazawa, S.Koso, K. Kunimori, K. Tomishige. Development of Ru/C catalyst for glycerol hydrogenolysis in combination with an ion-exchange resin. *Applied Catalysis A: General*:, vol. 318 , pp 244-251, 2007

[15] F.M. John, F.S. William, E.S. Peter, D.B. Kenneth. Handbook of X-ray Photoelectron Spectroscopy. *Perkin-Elmer Corporation, Physical Electronics Division*. October 1992