EFFECT OF SUPPORT MATERIALS ON CATALYTIC ACTIVITY OF NANO RUTHENIUM CATALYST IN HYDROGENOLYSIS OF GLYCEROL

(Kesan Bahan Penyokong Terhadap Aktiviti Pemangkin Nano Ruthenium dalam Hidrogenolisis Gliserol)

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Abstract
A series of heterogenous catalysts based on supported ruthenium were prepared from RuCl₃ precursor by impregnation method. The effect of support materials (bentonite, TiO₂, Al₂O₃ and SiO₂) on catalytic activity of Ru catalyst for hydrogenolysis of glycerol were investigated under mild reaction condition of 150°C and 20 bar initial hydrogen pressure for 7 hours reaction time and glycerol concentration was 20%(wt). It was found that the type of support material have significant effects on the activity and selectivity of glycerol hydrogenolysis. The order of Ru catalyst activity was Ru/bentonite > Ru/Al₂O₃ ≈ Ru/TiO₂ > Ru/SiO₂. This study showed that bentonite supported Ru catalyst was the most active with glycerol conversion reaching 62.5% compared to other supports. All the tested catalyst exhibited high selectivity to 1,2-propanediol with more than 80%. Characterization of the catalysts was carried out using BET, XPS, FESEM-EDX and TEM to obtain the physicochemical properties of the catalysts.

Keywords: hydrogenolysis, ruthenium, bentonite, 1,2-propanediol, glycerol

Introducation
Glycerol, one of the renewable resources, is obtained as a by-product in hydrolysis of fat, soap-manufacturing process and production of biodiesel [1]. Production of every 9 kg biodiesel, about 1 kg of crude glycerol by-product...
is formed [2]. 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. 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 [3]. 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 [4]. Typical uses of 1,2-propanediol are in unsaturated polyester resins, functional fluids, pharmaceuticals, cosmetics, paints and others [5]. Process that can efficiently convert glycerol to a useful compound would be important as an economical and sustainable process. Conversion of glycerol using supported catalyst has been extensively studied by several groups [6-9]. In published papers the effect of various supports (TiO$_2$, SiO$_2$, NaY, γ-Al$_2$O$_3$ and active –carbon) on Ru catalysts were investigated and found that the support material can influence the metal particles size.

Most of the previous studies have employed solid acid like carbon [2], alumina [10] and silica [8, 11] to be used for supporting the metal catalyst. Bentonite which has surface area about 100 m$^2$/g is natural clay raw material that has high content of montmorillonite and less amounts of other clay minerals. Previous report have shows that bentonite can be used as support material in catalytic reaction.[12, 13] They found that Ru-Cu bimetallic catalysts supported on clay exhibited 100 % of glycerol conversion and 85 % yield of 1,2-propanediol at 230°C and 8 MPa. Previous study by Yuan et al. claimed that solid base (hydrotalcite and MgO) supported Pt catalysts exhibited the predominant activity and higher 1,2-PDO selectivity than that of solid acids (Al$_2$O$_3$, H-ZSM5 and H-Beta)[14].

Since there are only a few studies focus on the application of solid base supported metal catalyst in hydrogenolysis of glycerol, therefore we want to report an efficient solid-base supported Ru catalyst for glycerol hydrogenolysis to 1,2-PDO. In this work, the effect of other support materials (Al$_2$O$_3$, SiO$_2$ and TiO$_2$) with bentonite material on catalytic performance of ruthenium (Ru) based catalysts in the hydrogenolysis glycerol were investigated. The scope of this study was to investigate the effect of support materials on the structure and physicochemical characteristics of the catalyst as well as the catalytic performance in the glycerol hydrogenolysis reaction.

**Materials and Methods**

**Chemicals**

Ruthenium chloride hydrate, RuCl$_3$.H$_2$O used as a metal precursor was purchased from Sigma. Aldrich. TiO$_2$, SiO$_2$ and Al$_2$O$_3$ used as support were purchased from Sigma, Aldrich. 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.

**Catalyst preparation**

All the supported were calcined in air at 500 °C for 3 hours before used to remove moisture and impurities. About 0.09 gram of RuCl$_3$ was dissolved in acetone and stirred for 15 minutes. Then, approximately 1.8 g of support was added into the resulting solution and sonicated for 1 hour. After that, the mixture was dried in oven at 60 °C overnight. The supported catalyst was calcined in N$_2$ flow (10 ml/min) at 300 °C for 2 hours and then reduced in H$_2$ flow (10 ml/min) at 200 °C for 2 hours.

**Catalyst characterization**

The X-ray photoelectron spectrum (XPS) data of the as-prepared samples were obtained by XPS Ultra from Kratos, UK using 300 W MgK $\alpha$ radiation. The base pressure was about 3 x 10$^{-9}$ mbar. The binding energies were referenced for 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 was 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.

**Catalytic reaction**

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 stirring speed. Before reaction started, the reactor was flushed three times with N\textsubscript{2} in order to remove oxygen gas and pressurized with H\textsubscript{2} to 20 bar.

**Results and Discussion**

The physical properties of prepared catalysts by BET nitrogen adsorption isotherm are presented in Table 1. The trend shows that BET surface area of supported catalyst increased following this order: Ru/TiO\textsubscript{2} < Ru/bentonite < Ru/SiO\textsubscript{2} < Ru/Al\textsubscript{2}O\textsubscript{3}. BET analysis revealed that BET surface area of Ru/bentonite was decreased drastically. It seems that about 65.8% of Ru particle was loaded into the mesoporous of bentonite. This result indicates that pore volume of bentonite was large and much Ru particle could load into pore of bentonite.

The isotherm plot revealed that the catalysts studied exhibited a very much similar types of isotherms, having a mixture of Type III and Type IV (Table 2). The isotherm plot displayed a hysteresis loop which is of the Type \textit{H2} according to the IUPAC classification. Type \textit{H2} indicating the presence of non-uniformed cylindrical pores.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Type of isotherms</th>
<th>Types of pores</th>
<th>Types of hysteresis</th>
<th>Shape of Pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/bentonite</td>
<td>IV</td>
<td>Mesopore</td>
<td>\textit{H2}</td>
<td>Non uniform cylindrical pore</td>
</tr>
<tr>
<td>Ru/TiO\textsubscript{2}</td>
<td>IV</td>
<td>Mesopore</td>
<td>\textit{H4}</td>
<td>Uniform slit shape</td>
</tr>
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<td>IV</td>
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<td>\textit{H4}</td>
<td>Uniform slit shape</td>
</tr>
<tr>
<td>Ru/Al\textsubscript{2}O\textsubscript{3}</td>
<td>III and IV</td>
<td>Mesopore and macropore</td>
<td>\textit{H3}</td>
<td>Non-uniform slit shape</td>
</tr>
</tbody>
</table>

Since XRD analysis did not show any peak related to Ru species except Ru/bentonite, therefore in order to investigate the presence of Ru species on the support, EDX analysis was done. Figure 1 clearly shows the existence of Ru species on the support.

The presence of Ru species was also indicated in the XPS wide scan and the binding energy (B.E) as shown in Table 3. The B.E of 280 and 283 eV is related to the chemical states of Ru\textsuperscript{0} and Ru\textsuperscript{II} respectively [15].
Table 3. XPS data for the supported catalyst

<table>
<thead>
<tr>
<th>Supported catalyst</th>
<th>Binding energy (eV)</th>
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<tbody>
<tr>
<td></td>
<td>C 1s</td>
</tr>
<tr>
<td>Ru/bentonite</td>
<td>284.8</td>
</tr>
<tr>
<td>Ru/TiO$_2$</td>
<td>284.8</td>
</tr>
<tr>
<td>Ru/SiO$_2$</td>
<td>284.8</td>
</tr>
<tr>
<td>Ru/Al$_2$O$_3$</td>
<td>284.8</td>
</tr>
</tbody>
</table>

Chemical state of the Ru element was investigated via narrow scan and the spectra are shown in Figure 2. Since the binding energy (B.E) of Ru 3d$_{5/2}$ ($\approx 280$ eV) overlapped with that C 1s ($\approx 284.5$ 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 (Ru$^0$ at 281.0 eV and Ru$^{4+}$ at 283.3 eV) except Ru species on bentonite shows chemical state of Ru$^0$ species only. Previous study have found that B.E of $\approx 283.0$ eV was assigned to RuO$_2$ which is corresponding to Ru$^{4+}$ species.$^9$ Meanwhile according to [3] the B.E value of Ru$^0$ species was in the range 280-281 eV.$^9$ The presence of Ru$^{4+}$ species indicated the Ru exists as oxide form and this species might be form during calcinations process.
Glycerol hydrogenolysis reaction

The effect of support materials on catalytic of 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 aqueous glycerol and catalyst loading used in this study are 20 %(wt) and 5 % respectively. The order of Ru catalyst activity was Ru/bentonite > Ru/Al₂O₃ ≈ Ru/TiO₂ > Ru/SiO₂. Figure 4 shows that Ru/bentonite catalyst was the most active catalyst which gave glycerol conversion reached 62.8 %. Good catalytic of Ru/bentonite is supported by TEM analysis since the average particle Ru/bentonite obtained was the smallest among the catalyst studied. Previous study reported that activity of Ru based catalyst was most active on smaller particle size of Ru. Mapping analysis by FESEM showed that dispersion of Ru particle was also related to the catalytic activity of Ru catalyst. Ru/bentonite which is most active was relatively more dispersed on bentonite support compared to other support. This result indicates that bentonite which has basic property support gave high conversion compared to acidic support (SiO₂, Al₂O₃ and TiO₂). Interestingly, Ru/bentonite also gave high selectivity to 1,2-propanediol (80.1 %) compared to other catalysts which are support on TiO₂, SiO₂ and Al₂O₃.
Figure 3. TEM image of (a) Ru/Al₂O₃, (b) Ru/Bentonite, (c) Ru/TiO₂, and (d) Ru/SiO₂

Furthermore, XPS analysis showed that RuO₂ species was reduced to Ru⁰ species completely on bentonite compared to other supports. This result indicates that Ru⁰ species was the active species that contributes the best
performance of Ru/bentonite catalyst. Surface area of Ru/bentonite analyzed by BET shows moderate BET surface area (35.4 m$^2$/g) compared to Ru/SiO$_2$ (131.0 m$^2$/g) and Ru/Al$_2$O$_3$ (141.0). However this does not indicate that the catalyst is not good for hydrogenolysis reaction because BET surface area is not the only factor that contributes to good catalytic activity of the catalyst. Other factors such as types and shapes of pore need to be considered [9].

From the catalytic result, there is a correlation between the types of pores with the activity of the catalyst. The catalyst with Type H2 (non-uniformed cylindrical pore) gave pores which have good catalytic activity with 62.8% conversion. The other catalysts with Type H4 (non-uniformed slit shaped) gave only around 10-35% conversion. As such we can assume that cylindrical pore is an ideal pore shape for hydrogenolysis glycerol reaction. This is because the adsorption and desorption process can easy to takes place in cyclindrical pore during hydrogenolysis glycerol.

**Conclusion**

It was found that the nature of support material greatly influence the performance of the supported Ru catalyst. A bentonite supported Ru catalyst (Ru/bentonite) exhibited the predominant activity and selectivity among the test catalyst and in a base-free aqueous solution under lower pressure. To best of our knowledge, Ru/bentonite system catalyst has not been reported yet for hydrogenolysis glycerol. Further study on the acidity and basicity of support has to be carried out.

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**References**