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## Effect of Calcination Temperature and Support Type of Pt/WO<sub>x</sub>/boehmite Catalyst on 1,3-propanediol Production from Hydrogenolysis of Glycerol

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# Effect of Calcination Temperature and Support Type of Pt/WO<sub>x</sub>/boehmite Catalyst on 1,3-propanediol Production from Hydrogenolysis of Glycerol

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**Abstract.** Hydrogenolysis of glycerol to 1,3-PDO was tested over different catalysts. To enhance 1,3-PDO selectivity, our work raised the calcination temperature from 800 °C to 900 °C that promoted Bronsted acidity, glycerol conversion and 1,3-PDO selectivity under the mild reaction condition (140 °C, 0.5 MPa). Glycerol conversion gradually raised from 32.8% to 36.6% and 1,3-PDO selectivity mildly increased from 18.2% to 21.2%. The loading of SiO<sub>2</sub> into Pt/WO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> had extremely favourable effects on 1,3-PDO selectivity because the amount of Bronsted acid sites increased significantly as confirmed by NH<sub>3</sub>-IR.

## 1. Introduction

Nowadays, the industrial manufacturing has a policy to promote the production of biodiesel from natural products in order to reduce the import of petroleum, in which the price is unpredictable and the loss of currency could be huge. The renewable biodiesel is an alternative energy, where its impact and significance have drawn tremendous interest both industrially and academically. Biodiesel can be made from various renewable sources such as plant oil, animal fat, waste cooking oil, etc.

Normally, biodiesel is acquired from the transesterification method of triglyceride (fat and oil) in which 90% of methyl ester (biodiesel) and 10% of glycerol are created. Likewise, glycerol can be produced from saponification process and hydrolysis reaction. It is in concern that huge amounts of glycerol are synthesized in biodiesel reaction. The transesterification process generated biodiesel and glycerol at a volumetric ratio of 10:1, so for every 1 m<sup>3</sup> of biodiesel, 0.1 of crude glycerol is obtained [1].

Glycerol is a valuable by product because it can be used in several applications for the industry. In the past, glycerol has more than two thousand different applications, especially in pharmaceuticals, personal care, foods and cosmetics. Glycerol is a nontoxic, edible, biodegradable feedstock. So, it will support significant environmental benefits to the new principles products. Glycerol is mainly used in the process of drugs, medicine and pharmaceuticals for the purpose of dissolving drug, giving the pills humidity and enhancement the viscosity of liquid drugs [2]. Glycerine or glycerol is an outstanding solvent of iodine, bromine, phenol, tannins, alkaloids, and mercury chloride [3]. Accordingly, all applications are not enough to manage amounts of surplus glycerol in global. Thus, the new valuable product is desired to get rid of an excess glycerol.

Essentially, new applications or new value-added products from glycerol must have been created by various pathways of chemical reaction. In the past, there were so many conversion processes of

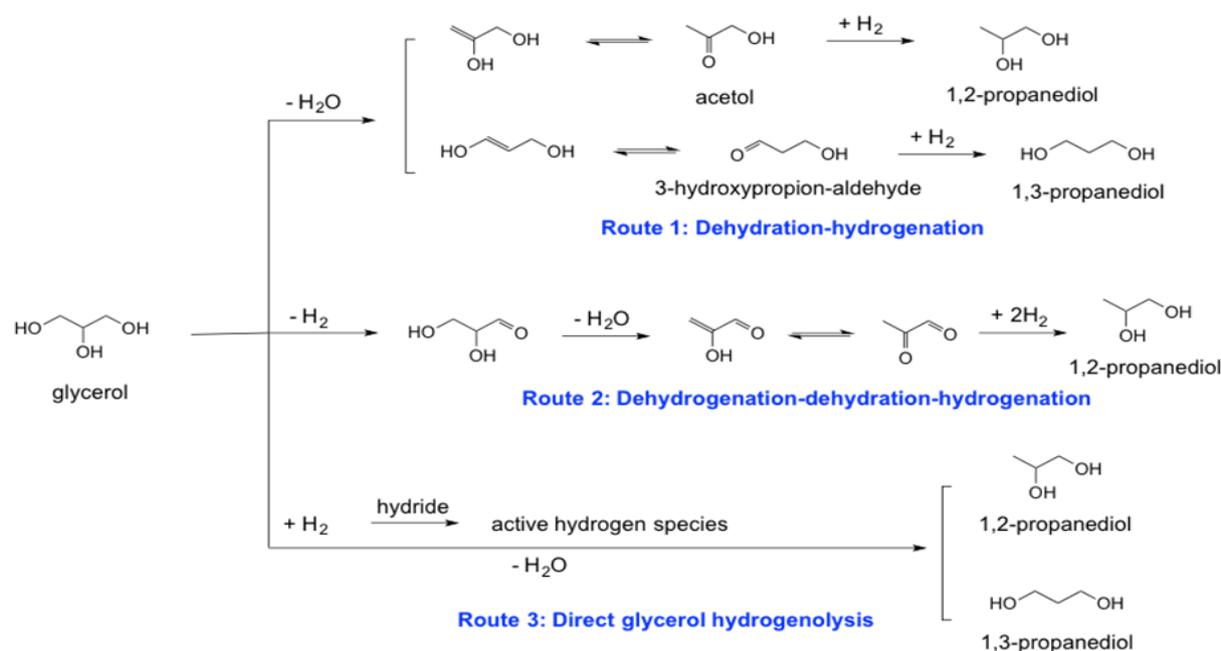


glycerol that have been reported including oxidation, dehydration, esterification, acetylation, reforming, hydrogenolysis, etherification, ammoxidation, acetalization and enzymatic reactions [4].

The entire products from alteration of glycerol, 1,3-propanediol and 1,2-propanediol are main products of hydrogenolysis reaction from glycerol because these two chemicals are essential substances in the process of synthesizing products or goods in the market. 1,2-propanediol is harmless chemical that can be synthesized and used as antifreeze deicing agents, pharmaceuticals, food, cosmetics, liquid detergents, flavorings and personal care products [5], since 1,3-propanediol can be used for various applications, especially as an intermediate to produce polymethylene terephthalate (PTT), polyether and polyurethane [6]. From the molecular structure, glycerol has one more –OH group than propanediol, so the hydrogenolysis reaction of glycerol to propanediol contains of the removal of one H<sub>2</sub>O and the addition of one H<sub>2</sub> molecule. The mechanism of hydrogenolysis reaction of glycerol can be divided into 3 types: dehydration-hydrogenation, dehydrogenation-dehydration-hydrogenation and direct glycerol hydrogenolysis [7]. Exactly, the mechanism should be specific, however it depends on the properties of catalyst used in reaction, such as the different acid-base catalysts, which can lead to different reaction mechanisms including the stability of intermediate in the reaction [8].

According to the literature, the hydrogenolysis catalysts have been applied in the hydrogenolysis reaction. It is found that there are two main functions to the selected catalyst for the hydrogenolysis reaction. First, the acidity or basicity of catalyst used to eliminate an OH-group. Mostly, metal oxides or acidic or basic support are used to provide acid-base function. The other one is the oxidation - reduction of hydrogen in the hydrogenolysis reaction. By the way, a lot of metals are also used as catalyst. It can be divided into 2 groups: transition metals (Cu, Ni, Co, etc.) [9-11] or noble metal (Pt, Ir, Ru, etc.) [12, 13]. Noble metals have remarkable properties in the oxidation-reduction reaction of hydrogen in the hydrogenolysis process. Kurosaka *et al.* reported that hydrogenolysis of glycerol reaction over Pt/WO<sub>3</sub>/ZrO<sub>2</sub> catalyst in DMI gave 28% selectivity to 1,3-propanediol at 86% conversion [14]. Zhu *et al.* using Pt-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> catalyst in aqueous phase at 200 °C, 6 MPa, showed 31.4% yield of 1,3- propanediol and 64.5% glycerol conversion [15]. Tao *et al.* carried out mesoporous WO<sub>3</sub> supported Pt catalyst afforded 18.0% conversion of glycerol and 39.2% selectivity for 1,3-propanediol [15]. In 2010-2012, Shinmi and Tomishige reported the use of Rh-ReO<sub>x</sub>/SiO<sub>2</sub> and Ir-ReO<sub>x</sub>/SiO<sub>2</sub> as catalysts for hydrogenolysis reaction of glycerol in water. The condition of reaction is 120 °C and 8 MPa. The result showed high yield of 1,3- propanediol. The mechanism of reaction is direct glycerol hydrogenolysis (route 3, scheme 1). Glycerol is adsorbed on surface of ReO<sub>x</sub> cluster at the terminal or middle position to generate 2,3-dihydroxypropoxide and 1,3-dihydroxypropoxide, respectively. Next, hydrogen activated on Ir metal attacks on 2-position of 2,3-dihydroxypropoxide to form 3-hydroxypropoxide. The hydrolysis of 3-hydroxypropoxide produces 1,3-propanediol. If hydrogen attacks on 3-position of 1,3-dihydroxypropoxide, the product will be 1,2- propanediol [16-18]. Quin *et al.* reported Pt/WO<sub>3</sub>/ZrO<sub>2</sub> catalyst at 130 °C and 4 MPa and showed a high yield of 1,3-propanediol (32%) [19]. Gong *et al.* obtained 15.3% glycerol conversion and 50.5% 1,3-propanediol selectivity over Pt/WO<sub>3</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> catalyst. [20]. In 2014, Kaneda *et al.* reported using Pt/WO<sub>3</sub>/“AlOOH” catalyst to obtain the highest 66% 1,3-propanediol because of the abundant of Al-OH groups in boehmite support [21].

From previous work, the hydrogenolysis reaction of glycerol was carried out at high pressure and temperature. So, our study was performed in mild condition and varied different supports by adding SiO<sub>2</sub> and different calcination temperatures of “AlOOH” (800 °C and 900 °C).



**Scheme 1.** The pathways of glycerol to propandiol by hydrogenolysis [22].

## 2. Experimental

### 2.1. Chemicals

1,3-propanediol (1,3-PDO), 1,2-propanediol (1,2-PDO) were purchased from Wako Pure Chemicals Co. Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ), glycerol, ammonium (Meta) tungstate were purchased from Sigma-Aldrich, colloidal silica and boehmite ( $\text{AlOOH}$ ) were obtained from the Taimei Chemicals Co. colloidal silica.

### 2.2. Catalyst preparation

Catalysts were prepared by wet-impregnation method. First, AMT 1.165 g was added to a 150 mL flask dissolved in 100 mL distilled water until AMT was completely dissolved and 10 g of boehmite was added to the solution and stirred at room temperature for 16 h. The catalyst product was separated by filtration and dried at 383 °C for 12 h. The solid catalyst was crushed into fine powder, following by calcination at 800 °C and 900 °C under a static air atmosphere for 3 h to get  $\text{WO}_x/\text{AlOOH}$  (White Powder).

2%Pt/ $\text{WO}_x/\text{AlOOH}$  was obtained from  $\text{H}_2\text{PtCl}_6$  0.216 mmol (0.103 g) dissolved in 50 mL distilled water in 100 mL flask and 2 g of boehmite-supported  $\text{WO}_x$  ( $\text{WO}_x/\text{AlOOH}$ ) was added to this solution, following by stirring at room temperature for 16 h, and then evaporation to dryness at 110 °C. The catalyst having pale yellow solid was crushed into fine powder and calcined at 300 °C under a static air atmosphere for 3 h. to obtain 2%Pt/ $\text{WO}_x/\text{AlOOH}$ .

Physical mixing between  $\text{SiO}_2$  calcined at 550 °C (1 g) and “AlOOH” calcined at 900 °C (1g) to obtain  $\text{SiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  support. Then, AMT (1.165g) solution was impregnated on  $\text{SiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  and dried at 110 °C for 12 h, following by calcination at 500 °C for 8 h. After that  $\text{WO}_x/\text{SiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  was impregnated with  $\text{H}_2\text{PtCl}_6$  0.216 mmol (0.103 g) to obtain 2%Pt/ $\text{WO}_x/\text{SiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  catalyst.

### 2.3. Catalytic reaction procedure

The hydrogenolysis reaction was performed in a 100 mL stainless steel autoclave equipped with Teflon vessel. Typically, 10 mmol of glycerol was added to 30 mL distilled water and 1.5 g of catalyst was placed in vessel. The reactor was stirred at 800 rpm, purged three times with  $\text{H}_2$  at 0.5 MPa, and then heated to 140 °C, pressurized to 0.5 MPa for 12 h. After that the reactor was cooled in an ice-water bath and the hydrogen gas was carefully released. The liquid product was analysed by GC

equipped with a flame ionization detector (FID) and a DB-WAX capillary column (30m x 0.32mm x 0.25um). Product analysis

The glycerol conversion and selectivity of product were calculated from the following equation:

$$\text{Conversion (\%)} = \frac{\text{Moles of introduced substrate} - \text{Moles of remained substrate}}{\text{Moles of introduced substrate}} \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{Moles of one product}}{\text{Moles of all product}} \times 100 \quad (2)$$

#### 2.4. Catalyst characterization

The X-ray diffraction (XRD) patterns were analyzed by X-ray diffractometer (Bruker D8 Advance) using Cu K $\alpha$  irradiation at range between 10 ° and 90 ° with a step of 0.05s-1. The lattice parameter and d-spacing were calculated based on Bragg's law. Crystallite size was calculated by Scherrer equation.

Scanning electron microscope (SEM), the elemental distribution on a surface of the catalysts was investigated with SEM-EDX using Link Isis series 300 program SEM (JEOL model JSM-5800LV).

IR spectra of ammonia adsorption were recorded with Bruker Vertex-70 FT-IR spectrometer equipped with a Harrick Praying Mantis attachment for diffuse reflectance spectroscopy. About 20–25 mg of sample was placed in a Harrick cell. The sample was heated to 500 °C at a heating rate of 10 °C/min under N<sub>2</sub> gas. Holding the temperature for 1 h under H<sub>2</sub>/N<sub>2</sub> gas. Then, the sample was heated to 550 °C at a heating rate of 10 °C/min under N<sub>2</sub> gas. The sample was cooled to 40 °C. After that the sample was saturated with 15% NH<sub>3</sub>/He for 30 min. The physisorbed ammonia was desorbed in a nitrogen gas flow about 1 h. The spectra were collected using a MCT detector.

### 3. Results and discussion

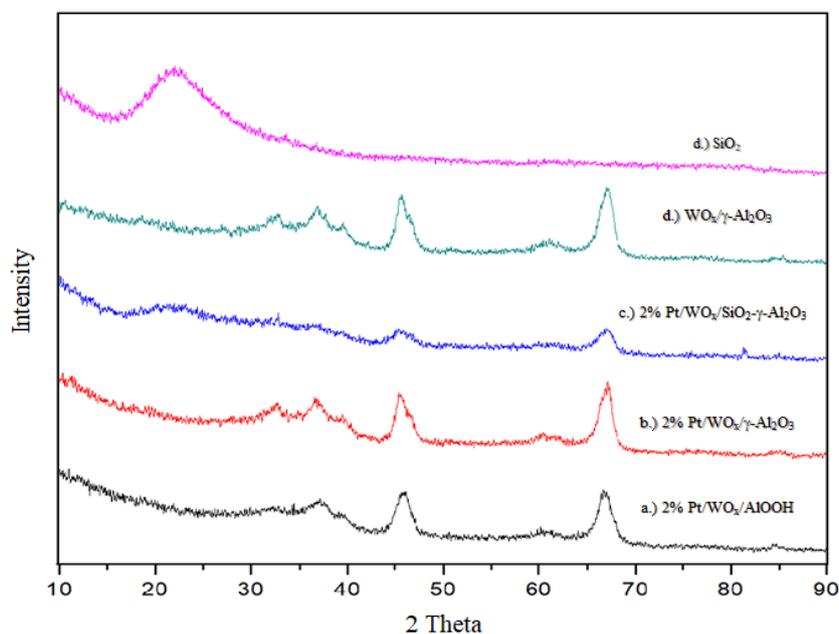
#### 3.1. Catalyst characterization

As seen in figure 1, the X-ray diffraction (XRD) patterns did not show any peaks of WO<sub>x</sub> species suggesting that tungsten was well dispersed over surface supports. The diffraction peaks of crystalline  $\gamma$ -alumina at  $2\theta = 37.5^\circ, 45.4, 66.9^\circ$  [24] were observed. Pt/WO<sub>x</sub>/AlOOH catalyst was not reduced in H<sub>2</sub>, so the peaks at  $2\theta$  values of  $46.6^\circ, 54.5^\circ$  and  $80.3^\circ$  were corresponding to PtO<sub>2</sub> [25].

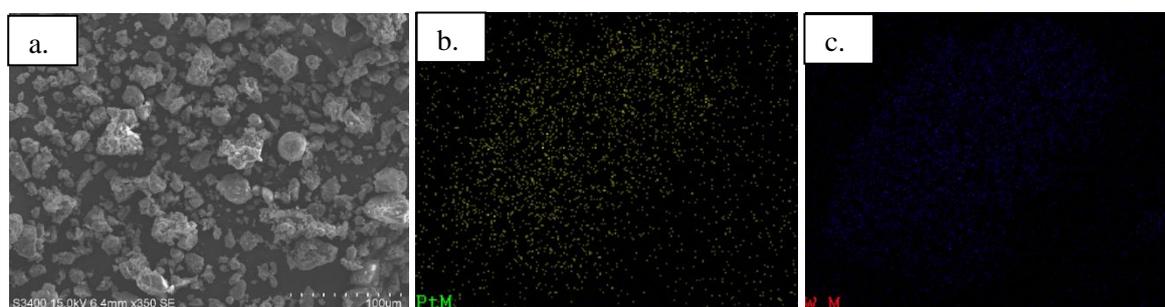
Figure 2. Shows the SEM image of Pt/WO<sub>x</sub>/AlOOH, catalyst that was highly crystalline. Pt and tungsten oxides have good dispersion on surface of support.

IR spectra of ammonia adsorption obtained after NH<sub>3</sub> adsorption are shown in Table 1. According to the literature [23], Bronsted and Lewis acid sites are simply identified and notable by examination of the 1100–1800 cm<sup>-1</sup> range. The band at 1454 cm<sup>-1</sup> is characteristic of symmetric deformation mode of the protonated NH<sub>3</sub> (NH<sub>4</sub><sup>+</sup>) coordinated to Brønsted acid. The band at 1260 cm<sup>-1</sup> is corresponding to the symmetric deformation mode of ammonia coordinated to Lewis acid sites. The total acidity is as follows; Pt/WO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Pt/WO<sub>x</sub>/SiO<sub>2</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Pt/WO<sub>x</sub>/AlOOH.

As shown in table 1, the addition of SiO<sub>2</sub> improved Bronsted acidity and the increase in calcination temperature from 800 °C – 900 °C enhanced Bronsted acidity as shown in figure 3.



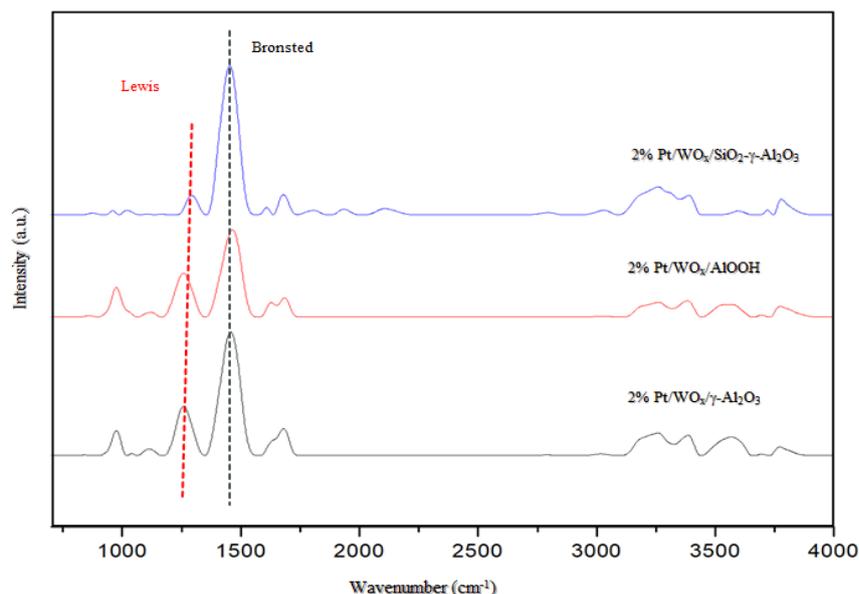
**Figure 1.** XRD patterns of a) fresh Pt/WO<sub>x</sub>/AlOOH, b) Pt/WO<sub>x</sub>/AlOOH used, c) WO<sub>x</sub>/AlOOH, and d) WO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub>



**Figure 2.** SEM image of a.) Fresh Pt/WO<sub>x</sub>/AlOOH catalyst, b.) Pt distribution, and c.) W distribution, obtained from SEM-EDX.

**Table 1.** The amounts of Bronsted and Lewis acid sites over the catalysts determined from the in situ DRIFTS of adsorbed NH<sub>3</sub>

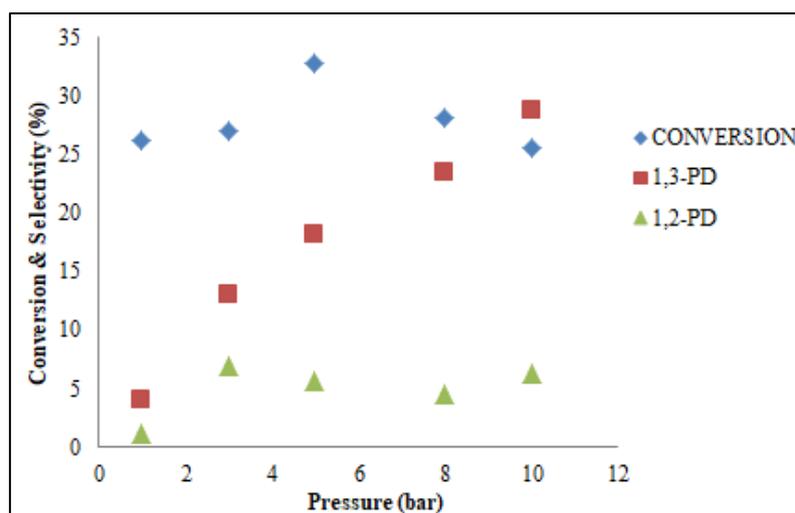
Catalyst	Lewis acid (a.u.)	Bronsted acid (a.u.)	B/L acidity	Total acidity (a.u.)
2%Pt/WO <sub>x</sub> /AlOOH	5.3	11.9	2.3	17.2
2%Pt/WO <sub>x</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	5.5	11.2	3.1	22.7
2%Pt/WO <sub>x</sub> /SiO <sub>2</sub> -γ-Al <sub>2</sub> O <sub>3</sub>	1.6	19.0	12.1	20.6



**Figure 3.** FTIR of adsorbed  $\text{NH}_3$  on fresh 2%Pt/ $\text{WO}_x$ /AlOOH (calcined at 800 °C), fresh 2%Pt/ $\text{WO}_x$ / $\gamma$ - $\text{Al}_2\text{O}_3$  (calcined at 900 °C) and 2%Pt/ $\text{WO}_x$ / $\text{SiO}_2$ - $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts

### 3.2. Influence of $\text{H}_2$ pressure

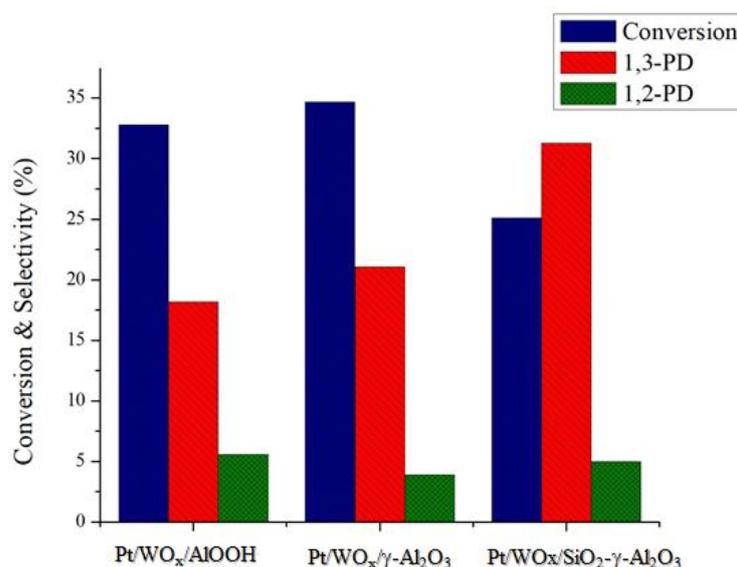
Figure 4. Illustrates the effect of  $\text{H}_2$  pressure on hydrogenolysis of glycerol over Pt/ $\text{WO}_x$ /AlOOH catalyst at 140 °C and 0.5 MPa, which is mildly condition. Glycerol conversion enhanced with increasing of  $\text{H}_2$  pressure in range from 0.1-0.5 MPa, associated with the increase of 1,3-PDO selectivity. There is no significant change of 1,2-PDO. The optimal glycerol conversion and selectivity of 1,3-PDO were 32.8% and 18.2% , respectively. In summary, the increase of 1,3-PDO may be due to enhanced hydrogenation rate and raise in the stimulate hydrogen species formed on Pt/ $\text{WO}_x$ /AlOOH catalyst.[15, 22]



**Figure 4.** Influence of initial hydrogen pressure on the hydrogenolysis of glycerol over the Pt/ $\text{WO}_x$ /AlOOH catalyst.

### 3.3. Influence of support to catalytic activity

Figure 5. Shows the experimental result of hydrogenolysis of glycerol over different catalysts. It was found that Pt/WO<sub>x</sub>/SiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalyst gave a remarkable 1,3-PDO selectivity (31.2% at 140° C, 0.5 MPa). According to result of NH<sub>3</sub>-IR, Pt/WO<sub>x</sub>/SiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> exhibited the highest Bronsted acid site leading to improved 1,3-PDO selectivity and silica has a strong affinity for glycerol, which was found in the etherification and esterification of glycerol reaction.[15, 20, 26, 27]. The different calcination temperatures affected to increased glycerol conversion and 1,3-PDO selectivity because total acidity and Bronsted acid site increased after calcined at 900 °C (34.6% glycerol conversion, 21.6% 1,3-selectivity). Bronsted acid site plays key role in dehydration of glycerol transfer to 3-HPA as an intermediate chemical in reaction. The hydrogenation of the intermediate on metal sites produces 1,3-PDO.[28]



**Figure 5.** Glycerol conversion and product selectivity obtained from hydrogenolysis of glycerol over different catalysts.

## 4. Conclusions

Our study has shown that the mild condition to carry out hydrogenolysis of glycerol reaction was selective to form 1,3-PDO depending on Bronsted acid site leading to high 1,3-PDO selectivity. The SiO<sub>2</sub> addition as support notably increased Bronsted acidity and H<sub>2</sub> pressure also influenced on the formation of 1,3-PDO.

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