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The effect of PO₄ to Nb₂O₅ catalyst on the dehydration of glycerol

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ABSTRACT

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Keywords: Glycerol Acrolein Niobium Phosphoric acid Liquid phase Dehydration The liquid-phase dehydration of glycerol to acrolein over PO_4/Nb_2O_5 catalysts was performed to investigate the effect of various amounts of PO_4 supported and the regeneration of used catalysts on catalytic performance. The amount of acid sites and strength of the surface acidity increased with the amount of PO_4 supported. Thus, these results seem to suggest that the amount of produced acrolein in the dehydration of glycerol is relatively influenced by the surface acidity of the catalysts used. Catalytic activity was restored by burning out of the surface deposited carbons in the used PO_4/Nb_2O_5 catalysts at 500 °C in air. However, it was not completely restored after regeneration for the 50 wt% PO_4/Nb_2O_5 catalyst due to the incomplete recovery of the drastically reduced surface acidity by the loss of the much resolved PO_4 during the reaction.

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1. Introduction

Glycerol is used as a component in industries such as food, medical supplies, petro chemistry, cosmetic, paint, and tobacco, and is produced from the biodiesel production process. With the increase in biodiesel production, the problem occurs of dealing with the surplus glycerol. It is therefore necessary to find new uses for glycerol. Glycerol is able to be transformed into valuable chemicals [1-3].

Acrolein is an important middle material used in a wide range of chemical materials such as acrylic acid, methionine, high absorbable polymer, detergent, etc. Acrolein is produced from propylene gas-phase oxidation with a mixed oxide catalyst. However, this process is highly affected by the oil price and releases large quantities of carbon dioxide in the air. Moreover, propylene is made from fossil fuel, the exhaustion of which is a concern. The need for an alternative production process to obtain acrolein from glycerol dehydration reaction is therefore gaining more attention. It is more economical and eco-friendly to apply glycerol than to use propylene as the feed for making acrolein [4,5].

The surface of metal oxide is mostly covered with hydroxyl group. The site that hydrogen is eliminated easily is bronsted acid

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site. Because electron concentration of exposed surface atom is lower than surrounding atom, the other site that is able to accept unshared electron pairs is Lewis acid site [6].

Metal oxide which has acid site on its surface is used widely for reactions needed acid catalyst, In case of glycerol dehydration for producing acrolein, mostly Al_2O_3 , SiO_2 , WO_3 , TiO_2 , ZrO_2 , Nb_2O_5 and etc. are used [5,7–10].

Fig. 1 shows the reaction path on glycerol conversion to acrolein in two dehydration steps. In the case of dehydration reaction, it is preferable to use a water resisting catalyst because of the high water formation in this reaction. It has also been reported that brønsted acid sites help produce more acrolein from glycerol.

 Nb_2O_5 is a well-known catalyst which has many brønsted acid sites, good water resistance and a large surface area. Nb_2O_5 is therefore a suitable solid acid catalyst as a supporter in the dehydration of glycerol to acrolein [11–13].

Through the glycerol polymerization process, heavy molecular weight materials can be produced such as 1,3-dioxolan-4-yl-methanol, 1,3-dioxan-5-ol, and 2-methyl-[1,3]dioxan-5-ol [5]. These cause carbon deposits and could decrease the catalyst activity by being absorbed on its active sites. These are by-products from the dehydration of glycerol. The by-product generation thus needs to be minimized to improve the efficiency of acrolein production while using the best catalyst for our purpose.

Here, we report the effect of various amounts of PO_4 loading to catalytic activity and acidity in the dehydration of glycerol to acrolein. We have found that PO_4/Nb_2O_5 made from Nb_2O_5 with





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Fig. 1. Glycerol dehydration to acrolein with acid catalyst.

loading PO_4 is an effective catalyst. The acidity and selectivity of acrolein is strengthened by increasing the PO_4 content.

2. Experimental

2.1. Catalyst preparation

 PO_4/Nb_2O_5 catalysts were prepared using the impregnation method with different PO₄ loadings in the range of 10–50 wt%. The required amount of H₃PO₄ (≥99.999% crystalline, Aldrich) was dissolved in distilled water, and the Nb₂O₅ (AD/1123, CBMM, Brazil) was added to the solution. The slurry was stirred for 1 h at 70 °C and evaporated under vacuum in a rotary evaporator until dry. The impregnated PO₄/Nb₂O₅ samples were dried at 100 °C for 6 h and calcined at 400 °C for 4 h.

2.2. Characterization of catalysts

The textural properties of prepared PO₄/Nb₂O₅ catalysts with different loadings that were derived from nitrogen physisorption isotherms on an ASAP 2020 instrument (Micromeritics Ins, U.S.A.) and PO₄ loading were measured using ICP-AES (OPTIMA 4300 DV, Perkin Elmer).

X-ray diffraction (XRD) patterns of the catalysts were obtained on a DMAX 100 (Rigaku, Japan) using Cu- $K\alpha$ radiation to measure their structural properties.

We conducted Temperature Programmed Desorption (TPD) analysis with a chemisorption analyzer (BEL-CAT, BEL, Japan) to measure catalyst acidity. The catalyst was pretreated in He condition at 250 °C for 1 h and cooled at 50 °C. NH3 was then adsorbed on the catalyst surface at a rate of 50 ml/min, for 70 min and the physically adsorbed NH3 was eliminated using He gas for 2 h. We made a TPD graph while increasing the temperature to 700 °C at 10 °C/min.

We used a thermo gravimetric analyzer (TGA) (METTLER TOLEDO, SKTA 851^e) to measure the amount of coke formed on the catalyst after the reaction. Increasing $10 \,^{\circ}$ C/min from room temperature to $1000 \,^{\circ}$ C in air condition, we calculated the coke deposit from the weight loss.



Fig. 2. XRD patterns of PO_4/Nb_2O_5 samples with different PO_4 loading. (a) 10 wt% PO_4/Nb_2O_5 , (b) 20 wt% PO_4/Nb_2O_5 , (c) 30 wt% PO_4/Nb_2O_5 , (d) 40 wt% PO_4/Nb_2O_5 and (e) 50 wt% PO_4/Nb_2O_5 .

2.3. Catalytic reaction

The liquid-phase dehydration of glycerol was carried out in a stainless autoclave reactor (Parr Instrument Co.) and reaction conditions were 240 °C under corresponding pressure, at a 300 rpm rotational speed and a 2 h reaction time. A 10 wt% aqueous glycerol solution of 70 ml and different PO_4/Nb_2O_5 catalysts of 4 g were used in all runs. The reaction products were condensed in a cold trap and analyzed by GC–MS (GCMS-QP-5000, Shimadzu).

3. Results and discussion

3.1. PO_4/Nb_2O_5 catalyst

3.1.1. Textural properties of catalysts

Table 1 presents the PO_4 loading measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) and the PO₄/Nb₂O₅ catalytic properties according to the loading of PO₄ obtained through N₂ physisorption. In accordance with the increased loading of the PO₄/Nb₂O₅ catalyst from 10 wt% to 50 wt%, the pores on the surface of Nb₂O₅ were clogged with the PO₄ particles; consequently, the surface area reduced from $83.6 \,\mathrm{m^2/g}$ to $3.1 \text{ m}^2/\text{g}$, and the pore volumes also gradually decreased from $0.13 \text{ cm}^3/\text{g}$ to $0.01 \text{ cm}^3/\text{g}$. When PO₄ was loaded at 30 wt% or more, the surface area reduced to $11.8 \text{ m}^2/\text{g}$ or less; this surface area was too small to measure pore size. At 50 wt%, the PO₄/Nb₂O₅ catalyst has a considerably small surface area of $3.1 \text{ m}^2/\text{g}$. While an increased wt% of PO₄ loading is thought to result in a reduced surface area, excessive PO₄ loading may not result in a desired and accurate PO₄ loading on Nb₂O₅. Therefore, experiments were conducted at a maximum 50 wt% of PO₄ loading.

3.1.2. Structural properties of catalysts

Fig. 2 presents changes in the structure of the PO_4/Nb_2O_5 catalyst according to PO_4 loading. No distinctive peak was observed at

Table 1

Textural properties of calcined PO₄/Nb₂O₅ catalysts.

Amount of loaded PO ₄ (wt%)	0	10	20	30	40	50
PO ₄ loadings (wt%) ^a	0	14	25	36	46	56
BET Surface area (m²/g) ^b	83.6	32.2	35.8	11.8	5.9	3.1
Pore volume (cm ³ /g) ^b	0.13	0.08	0.08	0.06	0.03	0.01

^a Determined by ICP-AES.

^b Determined by N₂ Physisorption.



Fig. 3. TPD profiles of PO_4/Nb_2O_5 samples with different PO_4 loadings. (a) Nb_2O_5 , (b) 10 wt%, (c) 20 wt% PO_4/Nb_2O_5 , (d) 30 wt% PO_4/Nb_2O_5 , (e) 40 wt% PO_4/Nb_2O_5 and (f) 50 wt% PO_4/Nb_2O_5 .

20 wt% or less of PO₄ loading, and a weak NbOPO₄ crystal peak was observed at 30 wt% or higher loading. In addition, at 40 wt% and 50 wt% PO₄/Nb₂O₅ catalysts, orthorhombic NbOPO₄ crystal structure was clearly observed around $2\theta = 20.7^{\circ}$, 24.3°, 29.1°, 36.1°, 46.9°, and 56.4°.

3.1.3. Acidic properties of catalysts

Changes in the surface acidity of the PO₄/Nb₂O₅ catalyst according to PO₄ loading was measured using the ammonia temperature-programmed desorption (TPD) method (Fig. 3). According to the TPD graph of Nb₂O₅ loaded with PO_4 (Fig. 3(b)–(f)), the peak area has increased overall upon loading PO₄. In the TPD curves, the peak area of ammonia desorption is associated with the amount of the acid site. As shown, the amount of acid site on the surface of the catalyst increased upon loading PO₄. In the case of 10 wt% PO₄/Nb₂O₅ catalyst, the peak area of ammonia desorption was confirmed to increase more at the range of 100-400 °C compared with the Nb₂O₅ catalyst. In the case of the 20 wt% PO_4/Nb_2O_5 catalyst, the peak was observed at a wide range of temperatures, and in the cases of 30 wt% and 40 wt% PO_4/Nb_2O_5 catalyst, a large ammonia desorption peak was observed at around 600 °C. In the case of 50 wt% PO₄/Nb₂O₅ catalyst, a very large ammonia desorption peak was observed in the 300-600 °C range, and a weak ammonia desorption peak was observed at 600 °C and above, even though the overlapped weak peak was not clearly seen. Overall, in accordance with the increase in PO₄ loading, the peak area is observed to increase, and the ammonia desorption peak moves from a low temperature range to a high temperature range. In the TPD curve, the ammonia desorption temperature is associated with acid strength. While the type of acid site is not clearly differentiated through TPD analysis, the approximate acid strength can be calculated by comparing ammonia desorption temperatures. A weak acid is considered to be the case in which a peak is observed in the range of 120–300 °C, while medium strength acid is considered to be a peak in the range of 300–500 °C, and strong acid at a peak in the range of 500–650 °C [7].

An Ammonia desorption peak appearing within a wide range of temperatures is usually observed in the case of PO_4 loading of 20 wt% or lower. In the case of 30 wt% or higher loading, the



Fig. 4. Effect of $\text{PO}_4/\text{Nb}_2\text{O}_5$ catalysts' amount of loaded PO_4 on glycerol conversion and acrolein selectivity.

amounts of medium strength acid and strong acid increased. The amount of strong acid site increased significantly compared with the catalysts with a 20 wt% or lower loading. In summary, as the amount of PO_4 loaded on Nb_2O_5 is increased, the amount of acid site and the acid strength also increase.

3.1.4. Catalytic activity

Fig. 4 presents the reaction activity of the PO_4/Nb_2O_5 catalyst according to PO₄ loading. In the case of the PO₄-loaded catalyst, acrolein selectivity noticeably increased compared with unloaded Nb₂O₅ catalysts. Particularly, in accordance with the increase in PO₄ loading, the glycerol conversion rate and acrolein selectivity increased. In the case of 50 wt% PO₄/Nb₂O₅ catalyst, the glycerol conversion rate was 68.1% and the acrolein selectivity was 72%, showing the highest catalyst activity. Under the same reaction condition, a 50 wt% PO₄/Al₂O₃ catalyst was prepared using lowactivity Al₂O₃ for the formation of acrolein, and a dehydration reaction of glycerol was conducted. As a result, the glycerol conversion rate was 24.8%, and the acrolein selectivity was 41.0%, despite the high amount of PO₄ loading. Based on the results, PO₄ did not directly affect the dehydration reaction of glycerol. In the case of the PO₄/Nb₂O₅ catalyst, a new active site is considered to be formed by the reaction between Nb₂O₅ and PO₄ in the process of preparing catalysts.

Nb₂O₅·*n*H₂O has a strong acidity ($H_0 \le -5.6$) which is equivalent to the acid strength of about 70% H₂SO₄. NbOPO₄ has higher acidity than Nb₂O₅·*n*H₂O ($H_0 \le -8.2$), which is equivalent to the acid strength of about 90% H₂SO₄ [14,15]. In the process of preparing the PO₄/Nb₂O₅ catalyst, Nb₂O₅ combines with PO₄, to form a NbOPO₄ crystal (Fig. 2). Since NbOPO₄ has very strong acidity, the activity of glycerol dehydration reaction is considered to be high compared with the Nb₂O₅ and PO₄/Al₂O₃ catalysts. In the case of the PO₄/Nb₂O₅ catalyst, increasing the amount of acid site on the surface and acid strength with the growing amount of PO₄ loaded on Nb₂O₅ (Fig. 3) has an effect on the glycerol conversion rate and acrolein selectivity toward high value.

3.2. Regeneration of PO₄/Nb₂O₅ catalyst after reaction

3.2.1. TG analysis

When strong acid catalysts are used in reactions, side reactions inducing carbon deposition on the surface of catalysts frequently occur. Carbon deposited on the catalyst surface disturbs the reaction on catalyst active sites and reduces catalyst activity.

Fig. 5 presents TG analysis data for comparing the amount of carbon deposition of the $50 \text{ wt\% PO}_4/\text{Nb}_2\text{O}_5$ catalyst before and



Fig. 5. TG curves of fresh and used catalysts.

after reaction. When compared with the TG curve of the catalyst before reaction, roughly 22 wt% of weight loss was observed in the catalyst at about 200–600 °C after reaction. The weight loss observed at about 200–400 °C is considered due to non-reacted glycerol remaining in the catalyst or large molecular products, and the weight loss observed at about 500 °C is considered due to the carbon deposition on the catalyst surface.

In order to regenerate the 50 wt% PO₄/Nb₂O₅ catalyst deposited with carbon after the reaction, calcination was conducted in the 400–700 °C range for 3 h in air atmosphere. TG analysis data on the catalysts according to regeneration temperature is shown in Fig. 6. In the case of the catalyst regenerated at 400 °C, roughly 5 wt% of weight loss was observed at about 500 °C. This result confirms that the carbon deposited on the surface of the catalyst which was regenerated at 400 °C was not completely burnt off. When the catalyst regenerated at 500 °C or above, almost no weight loss was observed. This result confirms that the carbon deposited on the surface of the surface of the catalyst which was regenerated at 500 °C or higher was observed. This result confirms that the carbon deposited on the surface of the catalyst which was regenerated at 500 °C or higher was burnt off.

3.2.2. Structural properties of catalysts

Fig. 7 shows XRD data on the 50 wt% PO_4/Nb_2O_5 catalyst before and after reaction, and after regeneration. In the case of the catalyst calcined before the reaction at 400 °C, an orthorhombic NbOPO₄ crystal peak was observed. By comparison, the catalyst after reaction showed a tetragonal NbOPO₄ crystal peak, and the regeneration catalyst showed a tetragonal NbOPO₄ crystal peak. This is because the crystalline state has changed in the hydrothermal



Fig. 6. TG curves of $50\,wt\%\,PO_4/Nb_2O_5$ catalysts regenerated at different temperatures.



Fig. 7. XRD patterns of various $50 \text{ wt\% PO}_4/\text{Nb}_2\text{O}_5$ samples. (a)fresh catalyst, (b) used catalyst, (c) regenerated catalyst.

reaction process to the more stable tetragonal NbOPO₄ crystal from the orthorhombic NbOPO₄ crystal. Based on these results, it was confirmed that the dehydration reaction of glycerol using the PO₄/Nb₂O₅ catalyst occurred at the tetragonal NbOPO₄ crystal.

3.2.3. Acidic properties of catalysts

Since catalyst activity is significantly affected by catalyst acidity in the dehydration reaction of glycerol, the acidity of the regeneration catalyst was measured (Fig. 8). Compared with the ammonia desorption peak of the 50 wt% PO₄/Nb₂O₅ catalyst before reaction (Fig. 8(d)), the ammonia desorption peak surface of the 50 wt% PO₄/Nb₂O₅ catalyst after regeneration has significantly decreased (Fig. 8(c)). By comparison, the difference in the ammonia desorption curve of the 20 wt% PO₄/Nb₂O₅ catalyst between the fresh catalyst and the regenerated catalyst was not significant, but a similar acidity was observed (Fig. 8(a)–(b)).

Regarding the PO_4 loading of the 20 wt% and 50 wt% PO_4/Nb_2O_5 catalysts measured using ICP before reaction and after regeneration (Table 2), the 20 wt% loading catalyst showed 25 wt% PO_4 loading



Fig. 8. TPD profiles of fresh and regenerated catalysts. (a) 20 wt% regenerated PO_4/Nb_2O_5 , (b) 20 wt% fresh PO_4/Nb_2O_5 , (c) 50 wt% regenerated PO_4/Nb_2O_5 , (d) 50 wt% fresh PO_4/Nb_2O_5 .

50 56

43

Table 2

PO₄ loadings of fresh and regenerated catalysts^a.

Amount of loaded PO4 (wt%)	20
Fresh catalyst (wt%)	25
Regenerated catalyst (wt%)	24

^a Determined by ICP-AES.

Table 3

Catalytic performance of various 50 wt% PO₄/Nb₂O₅^a.

	Fresh catalyst	Used catalyst	Regenerated catalyst
Conversion (%) Selectivity (%)	68.1	39.2	53.0
Acrolein	72	61.6	66.7
Acetaldehyde	8.4	8.6	8.9
Formic acid	0.9	2.0	1.9
Acetic acid	2.2	4.2	2.1
Acetone	3.1	4.6	4.3
2,3-Butanedione	9.5	5.0	3.4
Acrylic acid	1	1.0	3.0
Others ^b	2.9	13.0	9.7

 $^a\,$ Reaction conditions: Feed: 10 wt% glycerol 70 ml; Catalysts: 50 wt% PO_4/Nb_2O_5 4 g; Reaction temperature: 240 $^\circ$ C; Reaction time: 2 h.

^b Others contain methanol, ethanol, allyl alcohol, propanal, and several unidentified products.

before reaction and 24 wt% after regeneration, implying no significant difference. In contrast, the 50 wt% PO_4/Nb_2O_5 catalyst showed a significant PO_4 loss of 56 wt% before the reaction to 43 wt% after regeneration. This is because in the case of the 20 wt% PO_4/Nb_2O_5 catalysts, all PO_4 were combined with Nb_2O_5 to form $NbOPO_4$. However, the 50 wt% PO_4/Nb_2O_5 catalysts load an excess amount of PO_4 and PO_4 therefore remains on the $NbOPO_4$ that was formed by the combination of Nb_2O_5 and PO_4 that is loaded on the catalysts. In the case of the 20 wt% PO_4/Nb_2O_5 catalyst, Nb_2O_5 and PO_4 are well combined to avoid losing PO_4 during the reaction; however, in the case of the 50 wt% PO_4/Nb_2O_5 catalyst, an excess amount of PO_4 loaded on $NbOPO_4$ is dissolved during the reaction, resulting in the considerable loss of acid site. Consequently, the acidity of the 50 wt% PO_4/Nb_2O_5 catalyst before reaction sharply decreased from that of the catalyst before reaction.

3.2.4. Catalytic activity

Table 3 presents the dehydration reaction of the glycerol activity of the catalyst before and after reaction, and after regeneration. As a result of conducting the reaction using the catalyst which did not have a regeneration process after reaction, glycerol conversion rate was considerably low at 39.2%. This is due to the reduced catalyst acidity caused by the carbon deposition on the catalyst surface and the lost PO₄ during reaction. In the case of the regeneration catalyst, the glycerol conversion rate and acrolein selectivity were enhanced compared with those of the catalyst which was not regenerated. This is because the carbon deposited on the surface of the catalyst was burnt off during calcination in an oxygen atmosphere and the high temperature generating the catalyst regeneration effect. However, compared with the glycerol conversion rate of 66.8% before reaction, the glycerol conversion rate of the regeneration catalyst is lower at 53.0% due to the difference in acidity between the prereaction catalyst and the regeneration catalyst. The loaded PO₄ amount of the 20 wt% PO₄/Nb₂O₅ catalyst does not change after the reaction, while the 50 wt% PO₄/Nb₂O₅ catalyst loses significant PO₄ during the reaction, resulting in a sharp decrease in PO₄ after the reaction and accordingly, catalyst activity is not completely recovered in spite of the catalyst regeneration.

4. Conclusion

It was found that PO_4/Nb_2O_5 had high selectivity to produce acrolein from glycerol dehydration reaction. Especially, increasing the PO_4 content in Nb_2O_5 resulted in further acid sites on the catalyst surface and reinforced its acidity, which improved in the glycerol conversion and acrolein selectivity. The highest activity was observed in the 50 wt% PO_4/Nb_2O_5 , which was 68.1% glycerol conversion and 72.0% acrolein selectivity. The low activity of catalyst was caused by coke formation during the reaction, and the 50 wt% PO_4/Nb_2O_5 catalyst was regenerated in air condition at 500 °C and then recovered its activity compared to the non-regenerated catalyst. However, the catalyst could not be fully recovered because of the significant amount of PO_4 loss during reaction.

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