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Research Article

Influence of Phosphoric Acid Modification on Catalytic Properties of γ–χ Al_2O_3 Catalysts for Dehydration of Ethanol to Diethyl Ether

Mutjalin Limlamthong[1], Nithinart Chitpong[2], Bunjerd Jongsomjit[1,*]

[1]Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[2]Department of Textile Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathumthani, 12110, Thailand

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Abstract

In this present work, diethyl ether, which is currently served as promising alternative fuel for diesel engines, was produced via catalytic dehydration of ethanol over H_3PO_4-modified γ-χ Al_2O_3 catalysts. The impact of H_3PO_4 addition on catalytic performance and characteristics of catalysts was investigated. While catalytic dehydration of ethanol was performed in a fixed-bed microreactor at the temperature ranging from 200 ºC to 400 ºC under atmospheric pressure, catalyst characterization was conducted by inductively coupled plasma (ICP), X-ray diffraction (XRD), N_2 physisorption, temperature-programmed desorption of ammonia (NH_3-TPD) and thermogravimetric (TG) analysis. The results showed that although the H_3PO_4 addition tended to decrease surface area of catalyst resulting in the reduction of ethanol conversion, the Al_2O_3 containing 5 wt% of phosphorus ($5P/Al_2O_3$) was the most suitable catalyst for the catalytic dehydration of ethanol to diethyl ether since it exhibited the highest catalytic ability regarding diethyl ether yield and the quantity of coke formation as well as it had similar long-term stability to conventional Al_2O_3 catalyst. The NH_3-TPD profiles of catalysts revealed that catalysts containing more weak acidity sites were preferred for dehydration of ethanol into diethyl ether and the adequate promotion of H_3PO_4 would lower the amount of medium surface acidity with increasing catalyst weak surface acidity. Nevertheless, when the excessive amount of H_3PO_4 was introduced, it caused the destruction of catalysts structure, which resulted in the catalyst incapability due to the decrease in active surface area and pore enlargement.

Keywords: Ethanol Dehydration; Diethyl Ether; Phosphoric Acid; Heterogeneous Catalyst

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1. Introduction

In recent years, the reduction of oil supplies combined with the increase in pollutant emissions such as particular matters (PMs), volatile organic compounds (VOCs) and nitrogen oxide (NO_x) in the air through the combustion of fossil fuels has raised environmental concerns since it has been linked to resource depletion and adverse health effects. Therefore, alternative fuels such as bioethanol, which is based on renewable resources and can be easily attained via fermentation process of biomass, have then been employed instead of conventional fuels. Sun and Wang [1] pointed that bioethanol has received much attention owing to its sustainability and compatibility to traditional combustion engines,

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* Corresponding Author.
E-mail: bunjerd.j@chula.ac.th (B. Jongsomjit),
Telp: +66-22186874, Fax: +66-22186877

while conventional fuels which have high ethanol proportion are not widely used due to their corrosivity and water solubility problems resulting in detrimental effects to combustion engines and the fluctuation in fuel properties [1,2]. As a result, research trends then shift toward the use of ethanol in the production of value-added chemicals [3].

Ethanol can be converted into various chemicals mainly including ethylene and DEE through the following reactions:

(1) $2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$
$\Delta H_{(1),\ 298\ K} = -25.1$ kJ/mol

(2) $C_2H_5OH \rightarrow C_2H_4 + H_2O$
$\Delta H_{(2),\ 298\ K} = +44.9$ kJ/mol

Diethyl ether (DEE), one of the potential chemicals with high cetane number, currently receives a considerable interest as the substitution for transportation instead of diesel fuel. Considering its advantage, DEE is known for its low ignition temperature which is beneficial to solve cold-starting problems occurred when using ethanol as fuel [4]. According to the experiment of Jothi *et al.* [5], the reduction of NO_x, smoke and PMs was observed to be around 65%, 85% and 89%, respectively, during DEE adoption. Since DEE can be produced through catalytic ethanol dehydration reaction, various catalysts using via the reaction have been thoroughly studied [6-19].

With regard to catalysts, in spite of the fact that catalytic performance of zeolite catalysts is considerably high [11,20,21], they may be unstable during the process and are likely to be deactivated via the deposition of carbon [18]. As a result, alumina (Al_2O_3), which is currently applied as a significant catalyst in ethanol dehydration factory and has excellent stability, seems to be more applicable in the dehydration of ethanol. Also, from mentioned studies, it was found that surface acidity of catalysts strongly related to the strength of ethanol adsorption on acid sites, which contributed to the formation of different products [16]. Moreover, further understanding on the effects of catalysts characteristics on catalytic ability is still desirable. Presently, a number of studies are observed the catalytic activity of the first catalyst being used in the catalytic dehydration of ethanol to ethylene like phosphoric acid (H_3PO_4) [18,22]. According to journal articles of Ramesh *et al.* [13,19] and Zhang *et al.* [17], H_3PO_4 modification on H-ZSM-5 catalysts was found to highly improve selectivity toward both DEE and ethylene and catalytic stability; however, the selectivity was observed to greatly depend on H_3PO_4 content and reaction condition. Although, there is still no research referred to the incorporation of varied H_3PO_4 concentrations in Al_2O_3 catalyst.

The main aim of this present work is to investigate the effects of depositing H_3PO_4 in various concentrations on γ-χ Al_2O_3 catalysts through steady-state ethanol dehydration reaction to obtain the most suitable catalyst and optimal reaction condition for producing DEE. Therefore, in this study, the consequence of H_3PO_4 modification in terms of catalytic performance and catalytic stability on mixed γ- and χ-crystalline phase Al_2O_3 with γ/χ ratio of 1, which exhibited the highest catalytic activity among all nanocrystalline γ- and χ- Al_2O_3 catalysts as the study of Janlamool and Jongsomjit [23], had been investigated toward laboratory-scaled ethanol dehydration reaction to DEE. All catalysts were also characterized by inductively coupled plasma (ICP), X-ray diffraction (XRD), N_2 physisorption, temperature-programmed desorption of ammonia (NH_3-TPD), and thermal gravimetric (TG) analysis.

2. Materials and Methods

2.1 Catalyst Preparation

Mixed γ- and χ-crystalline Al_2O_3 catalyst was prepared by solvothermal technique, which has been described in the study of Wannaborworn *et al.* [24]. Briefly, 25 g of aluminum isopropoxide (Sigma Aldrich, 98%) was firstly dissolved in 100 cm^3 of a mixture between toluene (Merck, 99%) and 1-butanol (Fluka, 99%) with toluene/1-butanol volumetric ratio of 1. Thereafter, the mixture was put into an autoclave (300 cm^3) which already filled with 30 cm^3 of the same solvent as previously mentioned. After removing air impurities inside the autoclave by ultra-high purity nitrogen (Linde, 99.99%), the autoclave was heated up to 300 °C with a heating rate of 2.5 °C/min and then was held constantly for 2 h. Afterward, the solvent residues in the resulting solid were eliminated by using methanol, following by drying process at 110 °C overnight and calcination in synthetic air (Linde) at 600 °C for 6 h.

P-modified Al_2O_3 catalysts were prepared through acid activation technique by using various concentrations of H_3PO_4 (5-20%) obtained by dissolving the required amounts of H_3PO_4 (Carlo Erba, 98%) in deionized water. During the process, the Al_2O_3 catalyst was added to the prepared solutions and stirred thoroughly at room temperature for 30 min. The obtained precipitates were then dried at

110 °C overnight and finally were calcined in synthetic air (Linde) at 600 °C for 6 h. The phosphorous (P) contents were 5, 12, 14, and 20 wt%; thereby the resulting P-modified Al_2O_3 catalysts were denoted as $5P/Al_2O_3$, $12P/Al_2O_3$, $14P/Al_2O_3$, and $20P/Al_2O_3$, respectively.

2.2 Catalyst Characterization

The chemical composition of catalysts was determined by ICP, using Perkin Elmer OPTIMA 2000™ equipment. The crystalline phases of Al_2O_3 were identified by XRD technique, using SIEMENS D5000 with Cu-K_α radiation and Ni filter. The XRD patterns were recorded over the 2θ value of 10° to 80°.

Surface area and porous properties of catalysts were examined through N_2 adsorption-desorption at 77 K using Micromeritics ASAP 2000 automate equipment. Surface area was estimated from Brunauer-Emmett-Teller (BET) method, whereas pore volume and pore diameter were measured from Barrett-Joyner-Halenda (BJH) analysis.

Acid strength of catalysts was calculated from the NH_3-TPD profiles recorded by using Micromeritics Pulse Chemisorp 2750 instrument equipped with a thermal conductivity detector. Prior to the measurement, the samples were pretreated in a flow of helium at 200 °C for 1 h using a heating rate of 10 °C/min and then were cooled to the adsorption temperature of 40 °C. The adsorption of NH_3 (15%) was carried out for 30 min, following by physical desorption of NH_3 and temperature increment to 400 °C for chemical desorption of NH_3 with a heating rate of 10 °C/min.

The amounts of coke formation in used catalysts were determined by TG analysis, using TA Instruments SDTQ 600 analyzer. The temperature was increased from 100 °C to 800 °C with a heating rate of 10 °C/min.

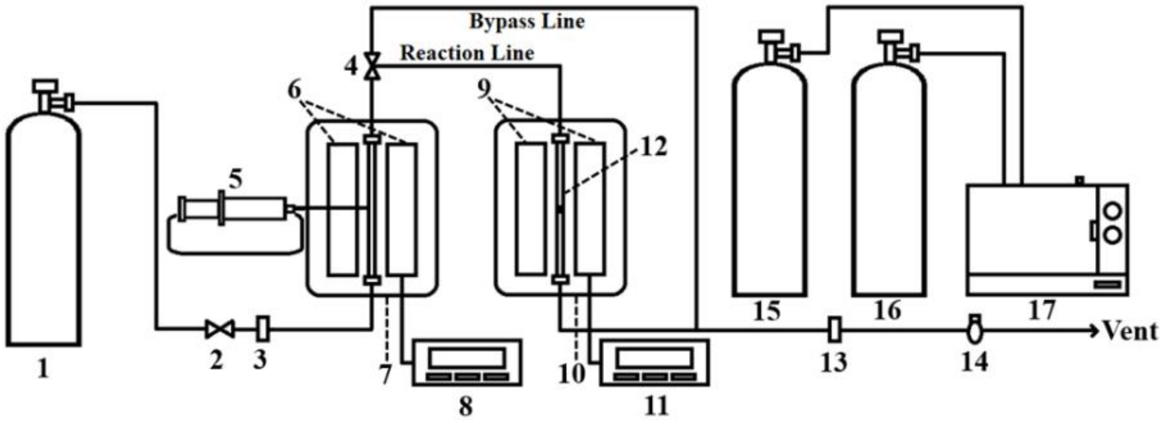
2.3 Catalytic Tests

Catalytic studies were performed in a fixed-bed borosilicate glass reactor (i.d. 7 mm.) under atmospheric pressure as depicted in Scheme 1. In a typical experiment, approximately 50 mg of each catalyst was loaded into the reactor and was activated in 50 mL/min of ultra-high purity nitrogen gas (Linde, 99.99%) at 200 °C for 1 h before the introduction of 10 mL/h of pure ethanol (Merck, 99.99%) into the reactor. The reactions were carried out at the reaction temperature ranging from 200 °C to 400 °C and stabilized for 1 h after each accretion. All products were analyzed both quantitative and qualitative values by Shimadzu GC-14A gas chromatography equipped with flame ionization detector (FID) and DB-5 capillary column. Additionally, the reactions were repeated for at least 3 times to confirm results' reliability. Ethanol conversion (X_{EtOH}), products selectivity (S_i), and products yield (y_i) were calculated from the results of chemical composition based on a mole basis via Equations (1), (2), and (3).

$$X_{EtOH} = \frac{n_{EtOH,i} - n_{EtOH,f}}{n_{EtOH,i}} \times 100 \qquad (1)$$

$$S_i = \frac{n_i}{\sum n_i} \times 100 \qquad (2)$$

$$y_i = \frac{X_{EtOH} S_i}{100} \qquad (3)$$



Scheme 1. Experimental setup for the continuous dehydration of ethanol. N_2 cylinder (1 and 15), on-off valve (2), mass flow controller (3), three-way valve (4), ethanol injector (5), thermal insulator (6 and 9), evaporation zone (7), temperature controller (8 and 11), reaction zone (10), glass reactor (12), collecting area (13), bubble flow meter (14), H_2 cylinder (16), gas chromatography: GC-14A (17)

3. Results and Discussion

3.1 Dehydration Reaction of Ethanol

The results of catalytic performance of Al_2O_3 and various P-modified Al_2O_3 catalysts toward the dehydration of ethanol under steady-state conditions are presented in Table 1 and depicted in Figures 1 and 2. According to the experimental data, it is apparent that while the ethanol conversion of all catalysts as well as both selectivity and yield of ethylene substantially enhanced with increasing reaction temperature, DEE showed excellent selectivity at the low reaction temperature below 300 ºC. With regard to the influence of H_3PO_4 addition on catalytic activities of catalysts, the results revealed that the higher P contents on catalysts could diminish total catalytic conversion at the reaction temperature lower than 300 ºC. On the other hand, ethanol conversion of catalysts considerably remained unchanged if the reaction occurred from 300 ºC to 400 ºC and the slight amount of H_3PO_4 was deposited. P contents were also found to be the active sites for DEE production as its selectivity dramatically rose when H_3PO_4 was introduced.

Table 1. Effect of reaction temperature and H_3PO_4 on ethanol conversion

Catalyst	Ethanol conversion (%)				
	200 ºC	250 ºC	300 ºC	350 ºC	400 ºC
Al_2O_3	14.1	40.1	60.4	84.9	88.5
$5P/Al_2O_3$	9.1	22.1	49.2	83.9	86.1
$12P/Al_2O_3$	8.1	19.3	40.0	61.9	72.9
$14P/Al_2O_3$	4.6	6.8	11.2	18.9	35.5
$20P/Al_2O_3$	0.0	0.0	3.5	9.6	17.2

Considering products yield, ethylene yield exhibited the similar trend as its conversion and selectivity since the highest ethylene yield of nearly 90% was achieved at high reaction temperature (400 ºC) over Al_2O_3 catalyst. A slight increase in P contents (5-12 wt% P), on the other hand, contributed to the downward trend of ethylene yield as well as the upward trend of DEE yield up to around one-third at

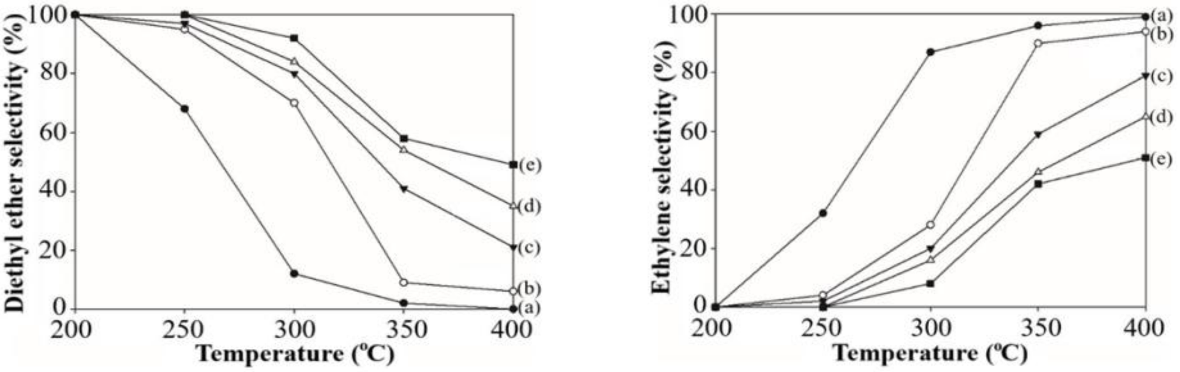


Figure 1. The percentage of diethyl ether and ethylene selectivity of Al_2O_3 and P-modified Al_2O_3 catalysts; (a) Al_2O_3, (b) $5P/Al_2O_3$, (c) $12P/Al_2O_3$, (d) $14P/Al_2O_3$ and (e) $20P/Al_2O_3$

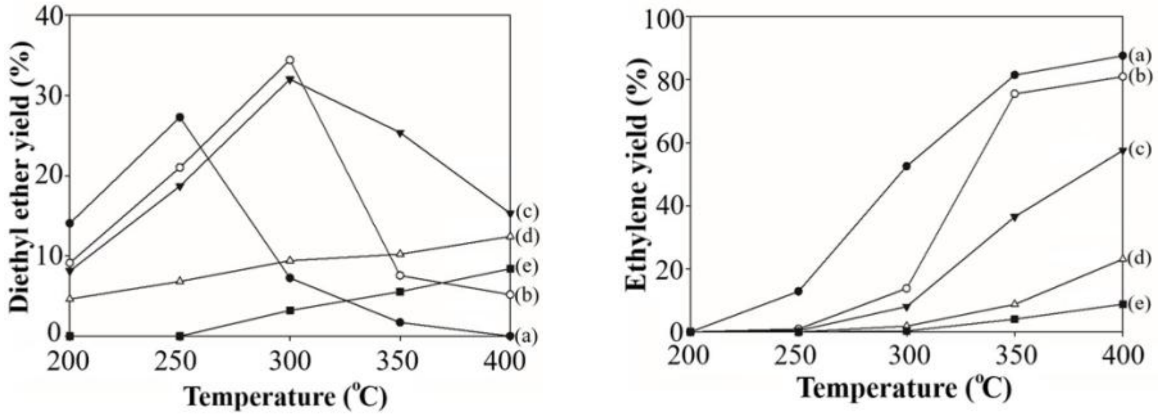


Figure 2. The percentage of diethyl ether and ethylene yield of Al_2O_3 and P-modified Al_2O_3 catalysts; (a) Al_2O_3, (b) $5P/Al_2O_3$, (c) $12P/Al_2O_3$, (d) $14P/Al_2O_3$, and (e) $20P/Al_2O_3$

300 °C. This indicated that the conventional catalyst, which can only produce the highest DEE yield of about a quarter, may not be suitable for DEE production, but was highly recommended for the manufacture of ethylene. P-modified Al_2O_3 catalysts still needed further development to improve their conversion at low reaction temperature for the production of DEE in industrial scales.

Since both Al_2O_3 and 5P/Al_2O_3 catalysts showed the similar ethanol conversion values at the reaction temperatures of 350 °C and 400 °C along with the highest DEE yield of 5P/Al_2O_3 catalyst was attained, both catalysts were brought to investigate their deactivation characteristics at the reaction temperature of 350 °C for 72 h. As illustrated in Figure 3, both catalysts presented their total conversion of ethanol just under 85% at the beginning of the study and remained unchanged along 72 h on stream. They also demonstrated the same values of DEE selectivity and yield as the general ethanol dehydration reaction under steady-state conditions as shown in Figures 1 and 2. Thus, it can be concluded that 5P/Al_2O_3 catalyst had a comparable long-term stability to the conventional catalyst.

3.2 Physicochemical Properties

The chemical composition, textural properties and surface acidity of Al_2O_3 and P-modified Al_2O_3 catalysts are listed in Table 2. In terms of textural properties, according to IUPAC classification of adsorption isotherms [25], all catalysts demonstrated the isotherm of type-IV. Also, a significant decrease in surface area and pore volume of catalysts was observed when P loadings were raised, which resulted from the partial pore blockage of P species during the acid activation process, contributing to the declination of overall conversion in the process.

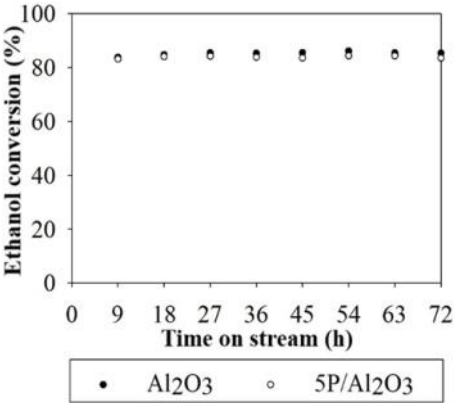


Figure 3. Ethanol conversion in dehydration of ethanol at 350ºC over Al_2O_3 and 5P/Al_2O_3 catalysts as a function of time

Considering pore diameter, the result revealed that doping with sufficient amount of H_3PO_4 led to the contraction of pore size. However, overloaded amount of H_3PO_4 (or in the case of the addition of 20 wt% of H_3PO_4) caused the rupture of pore due to the corrosivity of the modifying agent. This led 20P/Al_2O_3 catalyst to be incapable of transforming ethanol into any products as it demonstrated extremely low catalytic ability regarding ethanol conversion at all reaction temperatures. The data of pore size distribution is presented in Figure 4. It can be clearly seen that Al_2O_3, 5P/Al_2O_3, 12P/Al_2O_3 and 14P/Al_2O_3 samples exhibited pore diameter in a mesoporous range of 2-40 nm. On the other hand, 20P/Al_2O_3 catalyst illustrated the variation in pore size distribution within the mesoporous and macroporous size of 8-23 nm and 23-120 nm. This indicated the deformation of the catalyst structure, which confirmed the result of pore diameter.

Figure 5 shows XRD patterns of Al_2O_3 and various P-modified Al_2O_3 catalysts in the 2θ values ranging from 10° to 80°. XRD pattern of Al_2O_3 catalyst revealed both γ- and χ-crystalline phase as the investigation of Khom-in *et al.* [26]. In detail, γ-crystalline of conventional catalyst was observed at 2θ values of 32°, 37°, 46°, 61° and 67°, whereas χ-crystalline was detected at 2θ values of 37°, 43°, 46°, 61° and 67°. Regarding the modifying agent, XRD patterns of P-modified Al_2O_3 catalysts depicted the deposition of $AlPO_4$ species at 2θ values of 21°, 22° and 36° as the study of Rahmanian and Ghaziaskar [4]. Since Al_2O_3 and 5P/Al_2O_3 catalysts exhibited similar XRD patterns, it indicated that XRD can not detect the formation of $AlPO_4$ as a result of the formation of $AlPO_4$ with the size lower than 3-5 nm.

Figure 6 illustrates NH_3-TPD profiles of all catalysts in the temperature range of 50 °C to 400 °C. Surface acidity values of catalysts are also shown in Table 2. Acidity strength of catalysts received from the signal of NH_3 desorption below 300 °C (low-temperature; LT) and in a range of 300 °C to 400 °C (medium-temperature; MT) is considered as weak and medium acidity, respectively. In general, two desorption peaks were observed from the NH_3-TPD profile of Al_2O_3 catalyst. The increment of P contents in catalysts brought about the declination of medium surface acidity as well as the increase in weak surface acidity. However, from Figure 6, the results displayed the significant reduction of surface acidity in both LT and

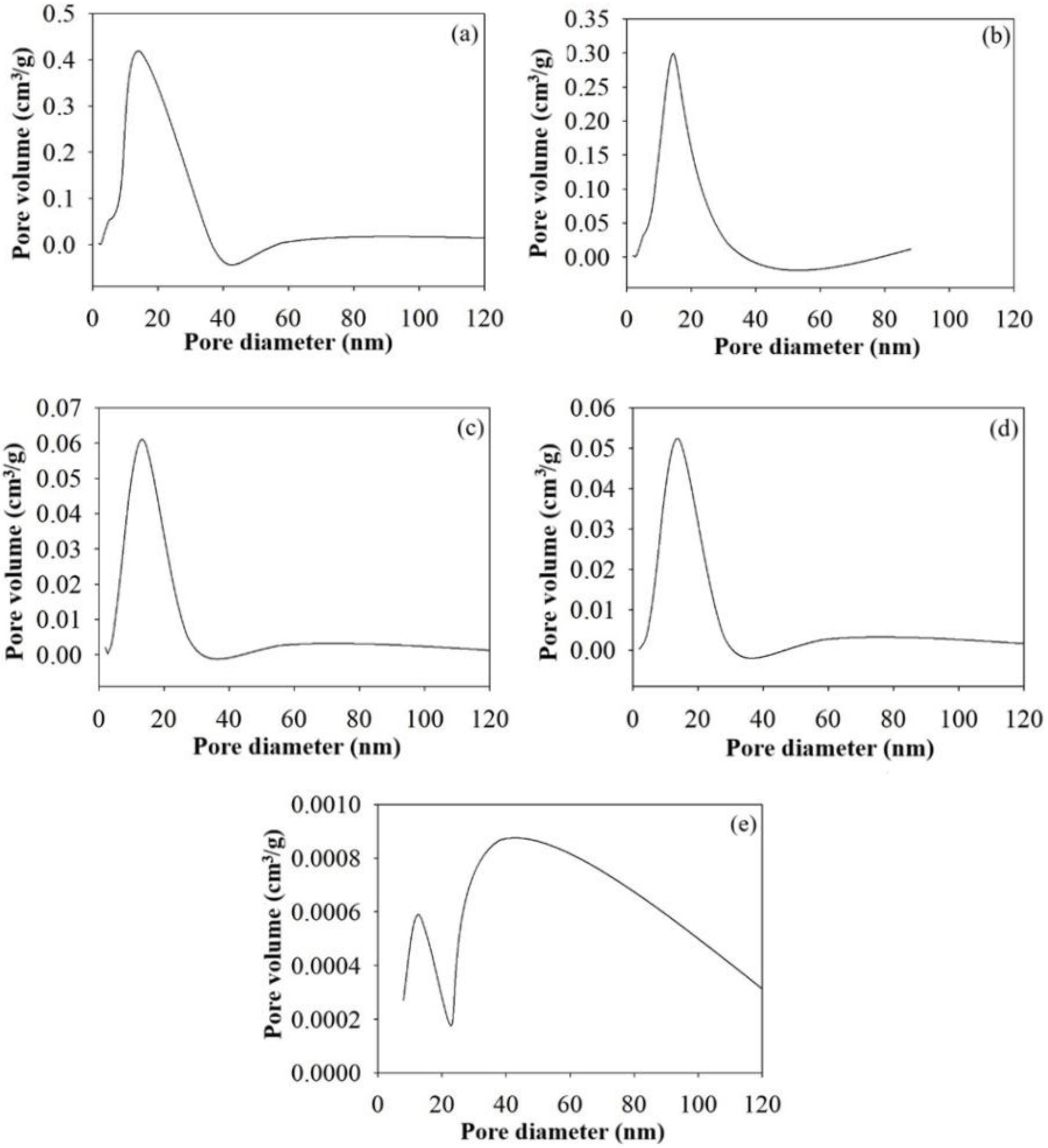


Figure 4. Pore size distribution of (a) Al_2O_3, (b) $5P/Al_2O_3$, (c) $12P/Al_2O_3$, (d) $14P/Al_2O_3$ and (e) $20P/Al_2O_3$

Table 2. Chemical composition, surface characteristics and surface acidity of fresh catalysts and the quantitative value of coke formation on used catalysts

Catalyst	P in bulk catalyst (wt%)	S_{BET} (m²/g)	V_p (cm³/g)	D_p (Å)	Surface Acidity (μmol/g)	Coke formation (%)
Al_2O_3	0	199	0.661	107.6	1230	4.56
$5P/Al_2O_3$	5	151	0.486	114.9	2620	2.51
$12P/Al_2O_3$	12	47	0.126	99.3	1170	1.11
$14P/Al_2O_3$	14	37	0.099	112.9	1100	0.93
$20P/Al_2O_3$	20	6	0.002	197.5	-	0.19

MT ranges after the introduction of H_3PO_4 higher than 5 wt%. This may be attributed to the deformation of catalysts structure owing to the addition of concentrated cautery. Therefore, 20P/Al_2O_3, which presented no surface acidity value signified the complete destruction of the catalyst structure, leading to the catalyst inefficiency. In addition, the result indicated that catalysts, which contained more weak acidity sites seemed to be more appropriate for producing DEE since 5P/Al_2O_3, the catalyst with the highest value of weak acidity, exhibited the highest percentage of selectivity toward DEE.

The quantity of coke formation on spent Al_2O_3 and P-modified Al_2O_3 catalysts is listed in Table 2. From the data, it is clear that the amount of coke generated on catalysts declined with the rise of P loadings. The results indicated that the addition of H_3PO_4 may lower catalytic activities in terms of ethanol conversion due to the partial clogging of the modifying agent on the surface of catalysts. Consequently, the decrease in ethanol conversion led catalysts to have less amount of coke formation. Nevertheless, 5P/Al_2O_3, which exhibited a comparable ethanol conversion to conventional catalysts was still promising for the future development since it had much lower quantity of coke formation on its surface compared to Al_2O_3 catalysts.

4. Conclusions

Although H_3PO_4 modification might lower ethanol conversion as it diminished surface area of catalysts, Al_2O_3 catalysts doped with 5 wt% of P is considered to be the most potential catalyst for the production of DEE through ethanol dehydration reaction and further developments in its capability in the future as it demonstrated the highest DEE yield with the lower amount of coke formation compared to conventional catalyst and had the comparable long-term stability to untreated Al_2O_3. Weak surface acidity sites were required for DEE production via ethanol dehydration reaction. The addition of appropriate H_3PO_4 concentrations contributed to the decline in medium surface acidity along with the escalation of weak surface acidity; however, the excessive amount of H_3PO_4 addition would damage the structure of catalysts resulting in the reduction of active surface area and pore cracking, which caused the inability of catalyst.

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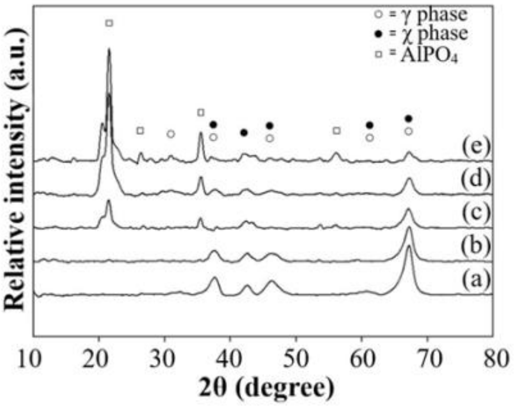

Figure 5. XRD patterns of (a) Al_2O_3, (b) 5P/Al_2O_3, (c) 12P/Al_2O_3, (d) 14P/Al_2O_3, and (e) 20P/Al_2O_3

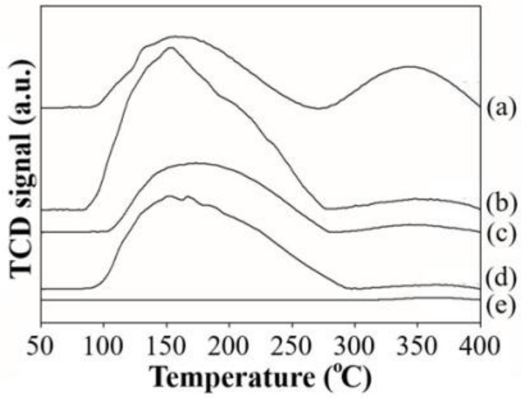

Figure 6. NH_3-TPD profiles of (a) Al_2O_3, (b) 5P/Al_2O_3, (c) 12P/Al_2O_3, (d) 14P/Al_2O_3 and (e) 20P/Al_2O_3

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