Characterization of Different Si- and Al-based Catalysts with Pd Modification and Their Use for Catalytic Dehydration of Ethanol
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Abstract: This study aims to investigate the production of ethylene and diethyl ether from ethanol via catalytic dehydration using Si- and Al-based catalysts with Pd modification. First, six catalysts including H-beta zeolite (HBZ), mixed phases of γ-χ-Al₂O₃ (M-Al) and γ-Al₂O₃ (G-Al) with and without Pd modification (0.5 wt%) were prepared. The catalytic dehydration of vaporized ethanol at temperature ranging from 200 to 400°C was performed over the catalysts. For ethylene production, the most promising catalyst is HBZ (giving ethylene yield of ca. 99% at 400°C), whereas Pd modification has no significant effect on ethylene production. Considering the production of diethyl ether, it is produced at lower temperature (ca. 250°C) than that of ethylene. The most active catalyst to produce diethyl ether is HBZ with Pd modification (giving diethyl ether yield of ca. 48% at 250°C). Thus, increased diethyl ether yield can be achieved with Pd modification at low temperature for the HBZ catalyst. Other catalysts such as M-Al and G-Al can also produce significant amounts of ethylene. To elucidate the effect of Pd modification on these catalysts, different characterization techniques such as nitrogen physisorption (BET and BJH methods), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and ammonia temperature-programmed desorption were performed and further discussed in more detail.

Key words: ethanol dehydration, ethylene, diethyl ether, Pd modification, Si-Al based catalysts

1 Introduction
In ancient times, the usage of fossil fuels such as higher hydrocarbon compounds for production of ethylene and diethyl ether (DEE) in thermal cracking at high temperature (600-1000°C) tends to create highly energy intensive and emissions of greenhouse gases. Many researchers agree that the renewable and eco-friendly biomass is interesting for alternative raw materials to produce other petroleum-based chemicals. At present, ethanol is one of the most important materials in the chemical industry because it can be used as feedstock to produce more valuable chemicals, especially ethylene and DEE. It is known that the catalytic ethanol dehydration has been considered as a benign alternative way to produce ethylene and DEE. This is because ethanol can be produced from fermentation of renewable feedstock (biomass) such as sugarcanes, molasses, corns, tapioca, etc. Thus, it can reduce environmental problem by decreasing the CO₂ emission from petrochemical-based feedstock. As known, the production of ethylene and DEE is interesting because both chemicals are used as raw materials to produce many products. For instance, ethylene is the starting material to produce a variety of products such as polyethylene, ethyl benzene, ethylene dichloride, and ethylene oxide. In addition, DEE is considered as a renewable fuel used to enhance the ignition property in diesel and gasoline engines, which presents high cetane and octane number and it is used to reduce NOx and smog emissions. Furthermore, DEE is also commonly used as a solvent in chemical processes for waxes, oils and production of plastics. In general, the catalytic dehydration of ethanol occurs in the temperature range of ca. 180°C to 500°C. This reaction mainly undergoes via two reaction pathways. Ethylene can be obtained by the endothermic reaction that is favored by moderate to high temperatures, whereas DEE can be achieved at lower temperature via the exothermic
reaction\textsuperscript{8, 11\textsuperscript{3\textsuperscript{3}} 17\textsuperscript{)}}. The catalytic dehydrogenation of ethanol essentially requires solid acid catalysts. Thus, acidity and acid strength are the key factors that influence on the catalytic behaviors. Many solid acid catalysts can catalyze this reaction mostly consist of silicon(Si) and aluminium(Al) as key elements\textsuperscript{8, 14}, such as zeolite\textsuperscript{3, 13, 15, 17}, alumina\textsuperscript{16}, montmorillonite clay\textsuperscript{17, 19}, silica and silica-alumina\textsuperscript{8, 12, 14}. For the best of our knowledge, zeolite and alumina catalysts have been found to be widely employed in this reaction due to their suitable character and high activity. These catalysts have been employed in ethanol dehydration reaction mostly consist of silicon(Si) and aluminium(Al) as key elements\textsuperscript{8, 14}, such as zeolite\textsuperscript{3, 13, 15, 17}, alumina\textsuperscript{16}, montmorillonite clay\textsuperscript{17, 19}, silica and silica-alumina\textsuperscript{8, 12, 14}.

Although, zeolites, especially for HZSM-5, show the less resistance of coke formation, they exhibit very high catalytic activity at low reaction temperature. Besides HZSM-5, other types of zeolite such as beta zeolites are captivating to employ in dehydrogenation reaction because they have proper acidic property and larger pore size leading to high resistance for the coke formation. The modification of zeolites to enhance the thermal stability were also widely investigated in previous studies\textsuperscript{8, 18}. Chemical promoters including metal oxides, alkali and alkaline earths, halogen groups and noble metals such as Rh, Ru, Pd, Pt, Re, Au, and Ir have been reported to exhibit high catalytic activity\textsuperscript{17, 20\textsuperscript{3\textsuperscript{3}} 22\textsuperscript{}}. Moreover, there are some works reported on the addition of chemical promoters including metal oxides\textsuperscript{8, 21\textsuperscript{3\textsuperscript{3}} 30} such as Mo, Zr, Ti, La, Ni, Fe, etc. We had demonstrated that both Ru and Pt can increase the catalytic activity and product yield, especially for diethyl ether\textsuperscript{27}.

This present research aims to determine the effect of palladium(Pd) modification as a chemical promoter on different solid acid catalysts for enhancement of the catalytic performance in ethanol dehydrogenation, especially to increase ethanol conversion and product yields at low reaction temperature. The Si- and Al-based catalysts including H-beta zeolite (HBZ), mixed phases of γ-χ-Al\textsubscript{2}O\textsubscript{3}(M-Al), and γ-Al\textsubscript{2}O\textsubscript{3}(G-Al) with Pd modification were studied. The effect of Pd modification on different catalysts is elucidated.

2 Experimental

2.1 Materials and catalyst preparation

The commercial H-beta zeolite (HBZ) catalyst having Si/Al molar ratio of 27 was purchased from Tosoh Corporation. The mixed phases of γ-χ-Al\textsubscript{2}O\textsubscript{3}(M-Al), γ-Al\textsubscript{2}O\textsubscript{3}(G-Al) catalysts were synthesized using the solvothermal method as reported by Janlamool and Jongsomjit\textsuperscript{19, 31}. Aluminum isopropoxide (AIP) and the mixture of toluene and 1-butanol with volume ratio of 1:1 as Al\textsubscript{2}O\textsubscript{3} precursor and organic solvent were used. The synthesis of M-Al was performed in an autoclave at 300°C for 2 h, and then the resulting powder was washed with methanol, dried and calcined in air at 600°C for 6 h. For γ-Al\textsubscript{2}O\textsubscript{3}(G-Al), it was prepared by calcination of aluminum nitrate nonahydrate at 700°C for 6 h. In addition, tetraamminepalladium(II) chloride monohydrate (99.99% Sigma-Aldrich Company Ltd.) was used as Pd source to promote on the catalysts above. The Pd precursor was directly impregnated onto the catalyst sample in order to have the Pd loading of 0.5 wt% in the final catalyst. After that, the Pd modified catalysts were dried overnight in oven at 110°C and calcined in air at 500°C for 2 h to obtain the Pd-modified catalysts (Pd-HBZ, Pd-M-Al and Pd-G-Al). Ethanol (99.99% Merck Company Ltd.) and ultra high purity nitrogen gas [99.99% Linde (Thailand) Public Company Ltd.] were used for the reaction study.

2.2 Catalyst characterization

The physicochemical properties of catalysts were determined by several techniques as follows:

- X-ray diffraction (XRD): XRD was used to determine the crystalline structure of catalysts. It was performed using a SIEMENS D-5000 X-ray diffractometer with CuK\textsubscript{α} (\(λ = 1.54439 \) Å). The XRD spectra were scanned at a rate of 2° min\textsuperscript{3\textsuperscript{3}} in the range of 2 theta degree = 10 to 90°.

- N\textsubscript{2} physisorption: N\textsubscript{2} physisorption\textsuperscript{3\textsuperscript{3}}(at −196°C) was used to measure the surface area (BET method). In addition, the average pore diameter and pore size distribution for all catalysts were determined by the BJH method. It was performed by a Micromeritics Chemisorb 2750 Pulse chemisorption system instrument. The adsorption and desorption isotherms were also obtained and used to identify the pore structures of catalysts.

- Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX): The morphology and elemental distribution of catalysts were investigated by SEM and EDX, respectively. The SEM images were obtained using Hitachi mode S-3400N. All micrographs were taken at the accelerating voltage of 30 kV and magnification ranging from 1,000 to 10,000 magnifications with resolution of 3 nm and the secondary scattering electron (SE) mode. Furthermore, EDX was used to determine the distribution of elements including Si, Al, O, and Pd on the external surface of catalyst granules. EDX was performed using Apollo X Silicon Drift Detector Series by EDAX.

- X-ray photoelectron spectroscopy (XPS): The binding energy of each core atomic orbital in the catalysts was determined by the AMICUS spectrometer using MgK\textsubscript{α} X-ray radiation (1253.6 eV) and AlK\textsubscript{α} X-ray radiation (1486.6 eV) at voltage of 15 kV and current of 12 mA. The pressure in the analysis chamber was less than 10\textsuperscript{−5} Pa. The small amount of sample was brought to pretreat at 110°C for 24 h before the analysis.

- Temperature-programmed desorption of ammonia (NH\textsubscript{3}-TPD): The acidity of catalysts was examined by NH\textsubscript{3}-TPD using Micromeritics Chemisorb 2750 pulse chemisorption system. In the experiment, 0.10 g of catalyst and 0.03 g of
quartz wool were packed in a U-tube glass, and then the catalyst sample was heated at 500°C in a flow of helium for 1 h. After that, the sample was saturated with 15% of NH3/He at 40°C for 30 min. To remove the physisorbed ammonia prior to the measurement, the catalyst sample was flushed under helium gas flow at 40°C for 30 min. Finally, the chemisorbed-ammonia was desorbed from the surface of catalyst under helium flow at temperatures ranging from 40 to 600°C. The amount of desorbed ammonia in the effluent as a function of desorbed temperature was detected by the TCD signal.

2.3 Reaction study

The catalytic ethanol dehydration was carried out in a borosilicate glass fixed-bed microreactor with an inside diameter of 0.7 cm and length of 33 cm. To perform the reaction study, 0.05 g of catalyst was packed into the middle of reactor. Then, the catalyst was heated in nitrogen (60 ml/min) to eliminate the humidity on surface of catalyst at 200°C for 1 h. A single syringe pump was used to control injection at a constant flow rate of liquid ethanol equals to 1.45 ml h⁻¹ (weight hourly space velocity (WHSV) = 22.9 (g_ethanol/g_cat) h⁻¹) through a vaporizer at 120°C. After that, the vaporized ethanol was fed into the reactor. The reaction was operated at the temperature ranging from 200 to 400°C under atmospheric pressure. The ethanol converted and remained, and products formed were analyzed by a Shimadzu GC 8A gas chromatograph with flame ionization detector (FID) using a capillary column (DB-5 (30 m × 0.25 mm × 0.25 μm)). The temperature of injector and detector for analysis were 150°C having nitrogen (pressure of 260 kPa) as carrier gas for gas chromatography (GC).

3 Results and discussion

3.1 Characteristics of catalysts

There were six catalysts including HBZ, M-Al and G-Al with and without Pd modification. All catalysts were characterized upon different techniques. First, the X-ray diffraction (XRD) patterns of all catalysts are shown in Fig. 1. The characteristic sharp peaks of HBZ catalyst are composed of 2θ at 14.6° and 22.4°, whereas the XRD peaks for chi phase of alumina (M-Al) are located at 37° and 43°, and 67° as also reported by Janlamoon and Jongsonjit31. When considered the effect of Pd modification on the catalysts, it revealed that peaks of Pd species did not appear because the Pd crystallites were present in a highly dispersed form and the loading amount of Pd is very low34, 35. The morphology of catalysts was obtained by scanning electron microscopy (SEM) and the results are presented in Fig. 2. The Pd-modified catalysts exhibited similar morphology with the corresponding unmodified ones. The Pd distribution on catalysts can be determined using EDX. The elemental distribution results from EDX analysis are illustrated in Table 1. This is used to measure the amounts of elemental composition near surface of catalysts. It was found that the amounts of Pd on surface of Pd-HBZ, Pd-M-Al and Pd-G-Al catalysts were 1.57, 2.10, and 1.72 wt%, respectively. This indicated that the amounts of Pd were slightly different on the outer surface of all catalysts.

The BET surface area (S_BET) was also examined by N₂ physisorption and the results are reported in Table 2. It revealed that the highest S_BET was found in HBZ (522 m² g⁻¹),
whereas G-Al showed the lowest surface area. This is because pore structure of alumina catalysts exhibits the mesoporous structure, while the zeolite has nearly boundary of micro- and mesoporous structures. Considering the effect of Pd modification on catalysts, it can be observed that Pd modification had only slight effect on Si- and Al-based catalysts. Figure 3 shows the results of pore structure for all catalysts, which were obtained from the N$_2$ adsorption-desorption isotherms. It indicates that all catalysts exhibited mesoporous structure according to Type IV as classified by IUPAC (International Union of Pure and Applied Chemistry). However, M-Al and Pd-M-Al also showed the characteristics of a hysteresis loop obtained over a range of high relative pressures, which is associated with capillary condensation of N$_2$ taking place in the presence of mesopores$.^8$ Besides the M-Al and Pd-M-Al, the N$_2$ sorption isotherms of other catalysts have a close similarity to type IV, although they perform the same characteristics of microporous structure as type I. The pore structure of all Pd-modified catalysts was only slightly different when compared with the unmodified ones. The position line of quantity adsorbed in Fig. 3 by the hysteresis loop for all catalysts has only slight difference.

XPS is one of the most powerful techniques to determine the surface properties of catalysts. Thus, the surface compositions on Pd-modified catalysts were analyzed by XPS technique. Considering the XPS spectra of Pd-modified catalysts (not shown), it is difficult to observe the binding energy peak of palladium due to its low amount. Nevertheless, some researchers such as Wang et al. and Niu et al. reported that the binding energies of Pd-modified catalysts are possibly observed between 338-339 eV (for Pd 3d$_{3/2}$) and 341-343 eV (for Pd 3d$_{5/2}$), corresponding to the binding energy of PdO$.^36,37$ Although the XPS result for Pd was not promising, the EDX technique can determine the existence and dispersion of palladium on Pd-modified catalysts as mentioned earlier. Thus, it is more conclusive to compare the XPS spectra of O 1s in different catalyst samples. The XPS spectra of O 1s for all samples are shown in Fig. 4.

After deconvolution, each O 1s spectrum can be divided into three kinds of oxygen species having the binding energy of 530.3, 532.2 and 533.9 eV indicating the lattice oxygen, surface hydroxyl groups and adsorbed oxygen mainly from adsorbed water molecules$.^8,19,38$ Moreover, three kinds of oxygen species exhibited the similar FWHM about 2 eV. The relative contents of different oxygen species on the surface of all catalysts were measured as shown in Table 3. The highest signal of hydroxyl groups (Fig. 4) and the amount of hydroxyl groups (Table 3) obtained from HBZ (ca. 73.8%) and Pd-HBZ (ca. 77.9%) were evident, which is related to the acidity as seen from the NH$_3$-TPD measurement. This phenomenon is also similar with other catalysts, where the amount of hydroxyl groups (50-54%) and total amount of acidity (1110-1198

### Table 1  Elemental distribution obtained from EDX.

| Catalysts | Si  | Al  | O   | Pd  | Si  | Al  | O   | Pd  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|
| HBZ       | 44.95 | 3.26 | 51.78 | 32.28 | 2.44 | 65.28 | 1.00 |
| Pd-HBZ    | 43.46 | 3.14 | 51.83 | 1.57 | 31.46 | 2.37 | 65.87 | 0.30 |
| M-Al      | 61.06 | 38.94 | 3.94 | 2.10 | 48.18 | 51.82 | 1.00 |
| Pd-M-Al   | 60.82 | 37.08 | 3.12 | 2.10 | 49.10 | 50.48 | 0.43 |
| G-Al      | 62.41 | 37.42 | 3.12 | 2.10 | 49.72 | 50.28 | 1.00 |
| Pd-G-Al   | 63.23 | 35.05 | 1.72 | 2.10 | 51.50 | 48.15 | 0.35 |

### Table 2  Properties of catalyst samples.

| Catalysts | BET Surface Area (m$^2$/g) | NH$_3$ desorption (µmol/g cat.) | Total acidity (µmol/g cat.) |
|-----------|-----------------------------|--------------------------------|----------------------------|
|           | Weak | Moderate to Strong            |                            |
| HBZ       | 522  | 844.8                         | 672.4                      | 1517 |
| Pd-HBZ    | 505  | 763.9                         | 737.9                      | 1502 |
| M-Al      | 195  | 386.2                         | 724.1                      | 1110 |
| Pd-M-Al   | 179  | 351.1                         | 845.2                      | 1196 |
| G-Al      | 119  | 396.0                         | 759.6                      | 1155 |
| Pd-G-Al   | 149  | 465.7                         | 733.0                      | 1198 |
μmolgcat⁻¹) were in the similar trend.

Temperature-programmed desorption (NH₃-TPD) was used to determine the acid strength and surface acidity of all catalysts. The acid strength of all catalysts can be measured by the desorption temperature of ammonia. The NH₃-TPD profiles of catalysts are shown in Fig. 5. For all catalysts, the profiles can be divided into two different types of surface acid sites following the position of desorption peaks. Many researchers noticed that the desorption peak below 250°C is referred to weak acid sites, whereas the moderate to strong acid sites are assigned from the ammonia desorption peak above 250°C.⁵,⁷, 24, 39 The characteristic peaks for each catalyst showed that the weak and moderate to strong acid sites have a significant difference in the quantity of acidic sites as depicted in Table 2. The number of acid sites on catalyst can be calculated by integration of desorption peak area of ammonia according to the Gauss curve fitting method. It indicated that the results of weak, moderate to strong and total acidity for all catalysts were not significantly affected by Pd modification. The highest acidity was obtained from HBZ and Pd-HBZ catalysts, especially in terms of the amount of weak and total acidity among those of other catalysts. It should be noted that HBZ and Pd-HBZ catalysts also showed the higher amount of weak acid than their moderate to strong acid sites. The types of acid site for both weak and strong acid sites, essentially affect the catalytic activity of ethanol dehydration⁴, 4⁰. In fact, the strong acid sites affect the catalyst deactivation because these sites can easily lead to produce higher hydrocarbon and coke formation¹, ²⁷.

### 3.2 Reaction study

Ethanol dehydration over all catalysts was investigated at reaction temperature from 200 to 400°C in order to determine the effect of Pd promoter on catalytic activity of various solid acid catalysts. Considering ethanol conversion in Fig. 6, it is shown that the ethanol conversion of catalysts increased with increasing the reaction temperature as expected. For the Pd modification over other solid acid catalysts, the modification with Pd tended to enhance the catalytic activity for all catalysts, especially at low reaction temperature (200-300°C) for Pd-HBZ and Pd-M-Al. However, the Pd-modified G-Al catalyst displayed the remarkable increase in ethanol conversion at high reaction temperature (350-400°C). When compared the activity of each catalyst, it was found that HBZ and Pd-HBZ exhibited
the highest ethanol conversion. This can be attributed to the evidence that HBZ and Pd-HBZ have the highest weak acid sites (Table 2), which is the key factor to enhance the catalytic activity in ethanol dehydration. Considering, the product selectivity for all catalysts (Fig. 7), it was found that the selectivity of ethylene increased with increasing the reaction temperature for all catalysts, whereas DEE selectivity decreased with increased temperature. However, the selectivity of acetaldehyde with Pd-modified catalysts tended to decrease with increasing temperature. According to the decreased DEE selectivity with high temperature, it is likely that ethanol is converted into other by-products such as acetaldehyde. This may be caused by the presence of Pd site on catalysts. Besides acetaldehyde, DEE can be cracked to ethylene at higher reaction temperature. As known, the ethanol molecule is adsorbed on surface catalysts to form ethoxy group, and then it interacts with second ethanol molecule, where DEE is obtained.

Fig. 4 XPS analysis for O 1s spectra of all catalysts.
The Ethanol Dehydration to Ethylene and Diethyl Ether over Different Si- and Al- based Catalysts

Table 3  XPS signals distribution of all catalysts.

| Catalysts | Binding energy for O 1s (eV) | O 1s area signals (%) |
|-----------|-------------------------------|-----------------------|
|           |                               | H₂O | OH  | O   |
| HBZ       | 533.6                         | 19.8| 73.8| 6.4 |
| Pd-HBZ    | 533.6                         | 14.3| 77.9| 7.8 |
| M-Al      | 532.8                         | 26.1| 50.3| 23.7|
| Pd-M-Al   | 531.7                         | 24.6| 54.5| 20.9|
| G-Al      | 533.2                         | 19.7| 55.5| 24.8|
| Pd-G-Al   | 533.1                         | 23.5| 54.6| 21.9|

in this step. Ethylene is mainly produced when reaction temperature increases by the direct mechanism of ethanol dehydrated to release ethylene. Moreover, DEE can be cracked to ethylene at high temperature resulting in increased selectivity of ethylene, whereas DEE selectivity decreased. In addition, the product yields of all catalysts are summarized in Table 4. It is interesting for the HBZ catalyst with Pd modification that DEE yield increased after Pd modification having the highest DEE yield of 48% at 250°C. Considering the Pd-modified M-Al and G-Al, it was found that the modification of Pd tended to enhance ethylene yield, especially at high temperature from 350 to 400°C. Meanwhile, the Pd modification on M-Al and G-Al catalysts resulted in increased ethylene yields compared with those of the unmodified catalysts. The highest ethylene yields of Pd-M-Al and Pd-G-Al catalysts (95% and 80%, respectively) were obtained under reaction temperature of 400°C.

In summary, upon the reaction test for all catalysts, it can be concluded that the addition of palladium into catalysts likely leads to enhance the catalytic activity and product yield, especially for the Pd-modified HBZ catalyst. This catalyst showed a remarkable increase in catalytic activity and DEE yield at temperature range of 200-300°C. Considering the effect of Pd modification on M-Al and G-Al, it was found that the ethylene yield at 300-400°C increased with Pd modification on these catalysts. It appears that Pd modification results in increased ethanol conversion, whereas it has only slight effect on the product selectivity. Based on XPS results, it is likely that increased amount of hydroxyl groups (binding energy of 532.2 eV for O 1s) with Pd modification is the main reason to enhance the catalytic activity. As mentioned in our previous study, the amount of hydroxyl groups is related to the acidity i.e.

Fig. 5  NH₃-TPD profile of all catalysts.
Bronsted sites. The effects of Ru and Pt modification on HBZ were also investigated in our previous work\(^\text{17}\). It revealed that the roles of noble metals on catalytic activity were quite similar, but Pd modification is the most promising promoter among other noble metals upon the production of both ethylene and DEE by catalytic dehydration of ethanol.

**Fig. 6** Ethanol conversion of all catalysts.

**Fig. 7** Product selectivity of all catalysts (a) HBZ and Pd-HBZ, (b) M-Al and Pd-M-Al and (c) G-Al and Pd-G-Al.

**Table 4** Ethanol conversion, product selectivity and product yield as a function of reaction temperature.

| Catalyst | Temperature (°C) | DEE (%) | CH\(_3\)CHO (%) | C\(_2\)H\(_4\) (%) |
|----------|------------------|---------|----------------|-----------------|
| HBZ      | 200              | 7       | 0              | 0               |
|          | 250              | 35      | 0              | 7               |
|          | 300              | 25      | 0              | 46              |
|          | 350              | 1       | 0              | 95              |
|          | 400              | 0       | 0              | 99              |
|          | 200              | 14      | 1              | 0               |
|          | 250              | 48      | 1              | 6               |
| Pd-HBZ   | 300              | 27      | 2              | 51              |
|          | 350              | 0       | 1              | 96              |
|          | 400              | 0       | 1              | 99              |
|          | 200              | 12      | 0              | 0               |
|          | 250              | 19      | 0              | 1               |
| M-Al     | 300              | 29      | 0              | 14              |
|          | 350              | 9       | 2              | 73              |
|          | 400              | 3       | 1              | 89              |
|          | 200              | 3       | 5              | 2               |
|          | 250              | 12      | 12             | 8               |
| Pd-M-Al  | 300              | 25      | 10             | 20              |
|          | 350              | 23      | 1              | 60              |
|          | 400              | 0       | 2              | 95              |
|          | 200              | 0       | 0              | 0               |
|          | 250              | 10      | 1              | 0               |
| G-Al     | 300              | 17      | 1              | 1               |
|          | 350              | 33      | 1              | 7               |
|          | 400              | 23      | 3              | 47              |
|          | 200              | 2       | 5              | 2               |
|          | 250              | 5       | 5              | 3               |
| Pd-G-Al  | 300              | 13      | 3              | 4               |
|          | 350              | 34      | 1              | 20              |
|          | 400              | 6       | 2              | 80              |
4 Conclusion

The Pd modification is able to increase the catalytic activity. For the HBZ catalyst, Pd modification had no significant effect on ethylene yield. However, it would appear that it had a significant effect on DEE yield and exhibited the highest DEE yield of 48% at 250°C. For the M-Al and G-Al catalysts, it can be concluded that the Pd modification can enhance ethylene yield at 400°C (95% and 80%, respectively), but it hardly affected the DEE yield. In addition, the Pd modification tended to increase acetaldehyde yield for M-Al and G-Al catalysts. Thus, the modification of solid acid catalysts with Pd is necessary to increase product yield for ethanol dehydration because it is able to act as the chemical promoter to increase the catalytic activity.

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References

1) Zhang, M.; Yu, Y. Dehydration of ethanol to ethylene. Ind. Eng. Chem. Res. 52, 9505-9514 (2013).
2) Sheng, Q.; Ling, K.; Li, Z.; Zhao, L. Effect of steam treatment on catalytic performance of HZSM-5 catalyst for ethanol dehydration to ethylene. Fuel Process. Technol. 110, 73-78 (2013).
3) Takahara, I.; Saito, M.; Inaba, M.; Murata, K. Dehydration of ethyl alcohol into ethylene over solid acid catalysts. Catal. Lett. 105, 249-252 (2005).
4) Xiao, Y.; Li, X.; Yuan, Z.; Li, J.; Chen, Y. Catalytic dehydrogenation of ethanol to ethylene on TiO2/4A zeolite composite catalysts. Catal. Lett. 130, 308-311 (2009).
5) Yu, M.; Li, J.; Chang, S.; Zhang, L.; Mao, Y.; Cui, T.; Yan, Z.; Luo, C.; Li, S. Bioethanol production using the sodium hydroxide pretreated sweet sorghum bagasse without washing. Fuel 175, 20-25 (2016).
6) Chen, B.; Lu, J.; Wu, L.; Chao, Z. Dehydration of bioethanol to ethanol over iron exchanged HZSM-5. Chin. J. Catal. 37, 1941-1948 (2016).
7) Chen, Y.; Wu, Y.; Tao, L.; Dai, B.; Yang, M.; Chen, Z.; Zhu, X. Dehydration reaction of bio-ethanol to ethylene over modified SAPO catalysts. J. Ind. Eng. Chem. 16, 717-722 (2010).
8) Soh, J.C.; Chong, S.L.; Hossain, S.S.; Cheng, C.K. Catalytic ethylene production from ethanol dehydration over non-modified and phosphoric acid modified Zelite H-Y catalysts. Fuel Process. Technol. 158, 85-95 (2017).
9) Feng, R.; Hu, X.; Yan, X.; Yan, Z.; Rood, M.J. A high surface area mesoporous γ-Al2O3 with tailoring texture by glucose template for ethanol dehydration to ethene. Microporous Mesoporous Mater. 241, 89-97 (2017).
10) Miller Jothi, N.K.; Nagarajan, G.; Renganarayanan, S. Experimental studies on homogeneous charge CI engine fueled with LPG using DEE as an ignition enhancer. Renew. Energy 32, 1581-1593 (2007).
11) Phung, T.K.; Busca, G. Diethyl ether cracking and ethanol dehydration: Acid catalysis and reaction paths. Chem. Eng. J. 272, 92-101 (2015).
12) Phung, T.K.; Busca, G. Ethanol dehydration on silica-aluminas: Active sites and ethylene/diethylether selectivities. Catal. Commun. 68, 110-115 (2015).
13) Madeira, F.F.; Gnepp, N.S.; Magnoux, P.; Maury, S.; Cadran, N. Ethanol transformation over HFAU, HBEA and HMFI zeolites presenting similar Bronsted acidity. Appl. Catal. A 367, 39-46 (2009).
14) Phung, T.K.; Proietti Hernández, L.; Lagazzo, A.; Busca, G. Dehydration of ethanol over zeolites, silica alumina and alumina: Lewis acidity, Bronsted acidity and confinement effects. Appl. Catal. A 493, 77-89 (2015).
15) Kamsuwon, T.; Jongsomjit, B. A comparative study of different Al-based solid acid catalysts for catalytic dehydration of ethanol. Eng. J. 20, 63-75 (2016).
16) Krutpjjit, C.; Jongsomjit, B. Catalytic ethanol dehydration over different acid-activated montmorillonite clays. J. Oleo Sci. 65, 347-55 (2016).
17) Kamsuwon, T.; Praserthdam, P.; Jongsomjit, B. Diethyl ether production during catalytic dehydration of ethanol over Ru- and Pt-modified H-beta zeolite catalysts. J. Oleo Sci. 66, 199-207 (2017).
18) Phung, T.K.; Lagazzo, A.; Rivero Crespo, M.Á.; Sánchez Escribano, V.; Busca, G. A study of commercial transition alumina and their catalytic activity in the dehydration of ethanol. J. Catal. 311, 102-113 (2014).
19) Janlamool, J.; Jongsomjit, B. Catalytic ethanol dehydration to ethylene over nanocrystalline ch and gamma-Al2O3 catalysts. J. Oleo Sci. 66, 1029-1039 (2017).
20) Wan Abu Bakar, W.A.; Ali, R.; Mohammad, N.S. The effect of noble metals on catalytic methanation reaction over supported Mn/Ni oxide based catalysts. Arab. J. Chem. 8, 632-643 (2015).
21) Yuan, C.; Liu, H.; Zhang, Z.; Lu, H.; Zhu, Q.; Chen, Y. Alkali-metal-modified ZSM-5 zeolites for improvement of catalytic dehydration of lactic acid to acrylic acid. Chin. J. Catal. 36, 1861-1866 (2015).
22) Yang, C.; Zhang, Q.; Li, J.; Gao, R.; Li, Z.; Huang, W.
Catalytic activity and crystal structure modification of Pd/γ-Al2O3–TiO2 catalysts with different Al2O3 contents. J. Energy Chem. 25, 375-380 (2016).

23) Phung, T.K.; Proietti Hernández, L.; Busca, G. Conversion of ethanol over transition metal oxide catalysts: Effect of tungsta addition on catalytic behaviour of titania and zirconia. Appl. Catal. A 489, 180-187 (2015).

24) Han, Y.; Lu, C.; Xu, D.; Zhang, Y.; Hu, Y.; Huang, H. Molybdenum oxide modified HZSM-5 catalyst: Surface acidity and catalytic performance for the dehydration of aqueous ethanol. Appl. Catal. A 396, 8-13 (2011).

25) Chinniyomphanich, U.; Wongwanichsin, P.; Jitkarnka, S.; Sn xOy/SAPO-34 as catalysts for catalytic dehydration of bio-ethanol: impacts of oxidation state, interaction, and loading amount. J. Clean. Prod. 111, 25-33 (2016).

26) Sujeerakulkai, S.; Jitkarnka, S. Bio-based hydrocarbons and oxygenates from catalytic bio-ethanol dehydration: comparison between gallium and germanium oxides as promoters on HBeta zeolites with various silica to alumina ratios. J. Clean. Prod. 111, 51-61 (2015).

27) Masiran, N.; Vo, D.-V.N.; Salam, M.A.; Abdullah, B. Improvement on coke formation of CaO-Ni/Al2O3 catalysts in ethylene production via dehydration of ethanol. Procedia Eng. 148, 1289-1294 (2016).

28) Gobara, H.M.; Mohamed, R.S.; Hassan, S.A.; Khalil, F.H.; El-Sall, M.S. Pt and Ni nanoparticles anchored into metal–organic frameworks MIL-101 (Cr) as swift catalysts for ethanol dehydration. Catal. Lett. 146, 1875-1885 (2016).

29) Kozłowski, J.T.; Davis, R.J. Sodium modification of zirconia catalysts for ethanol coupling to 1-butanol. J. Energy Chem. 22, 58-64 (2013).

30) Gayubo, A.G.; Alonso, A.; Valle, B.; Aguayo, A.T.; Olayar, M.; Bilbao, J. Hydrothermal stability of HZSM-5 catalysts modified with Ni for the transformation of bioethanol into hydrocarbons. Fuel 89, 3365-3372 (2010).

31) Janlamool, J.; Jongsomjit, B. Oxidative dehydrogenation of ethanol over AgLi–Al2O3 catalysts containing different phases of alumina. Catal. Commun. 70, 49-52 (2015).

32) Jansen, J.C.; Creyghton, E.J.; Njo, S.L.; Koningsveld, H.V.; Bekkum, H.V. On the remarkable behaviour of zeolite Beta in acid catalysis. Catal. Today 38, 205-212 (1997).

33) Khom-in, J.; Praserthdam, P.; Panpranot, J.; Mekasuwandumrong, O. Dehydration of methanol to dimethyl ether over nanocrystalline Al2O3 with mixed γ- and χ-crystalline phases. Catal. Commun. 9, 1955-1958 (2008).

34) Pillai, U.R.; Sahle-Demessie, E. Strontium as an efficient promoter for supported palladium hydrogenation catalysts. Appl. Catal. A 281, 31-38 (2005).

35) Phung, T.K.; Radikapratama, R.; Garbarino, G.; Lazzaro, A.; Riani, P.; Busca, G. Tuning of product selectivity in the conversion of ethanol to hydrocarbons over H-ZSM5-based zeolite catalysts. Fuel Process. Technol. 137, 290-297 (2015).

36) Wang, L.; Wang, F.; Wang, J. Effect of K promoter on the stability of Pd/NFY catalysts for acetylene hydrochlorination. Catal. Commun. 83, 9-13 (2016).

37) Niu, S.; Guo, W.; Lin, T.-W.; Yu, W.; Wu, Y.; Ji, X.; Shao, L. Nanoscale Pd supported on 3D porous carbon for enhanced selective oxidation of benzyl alcohol. RSC Adv. 7, 25885-25890 (2017).

38) Martins, L.; Cardoso, D.; Hammer, P.; Garetto, T.; Pulcinelli, S.H.; Santilli, C.V. Efficiency of ethanol conversion induced by controlled modification of pore structure and acidic properties of alumina catalysts. Appl. Catal. A 398, 59-65 (2011).

39) Pang, Y.; Su, X.; Bai, X.; Wu, W.; Wang, G.; Xiao, L.; Yu, A. Aromatization over nanosized Ga-containing ZSM-5 zeolites prepared by different methods: Effect of acidity of active Ga species on the catalytic performance. J. Energy Chem. 26, 768-775 (2017).

40) Takahara, I.; Saito, M.; Matsuhashi, H.; Inaba, M.; Murata, K. Increase in the number of acid sites of a H-ZSM5 zeolite during the dehydration of ethanol. Catal. Lett. 113, 82-85 (2007).

41) Zhan, N.; Hu, Y.; Li, H.; Yu, D.; Han, Y.; Huang, H. Lanthanum–phosphorous modified HZSM-5 catalysts in dehydration of ethanol to ethylene: A comparative analysis. Catal. Commun. 11, 633-637 (2010).