Ethylene Formation from Ethanol Dehydration Using ZSM-5 Catalyst
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ABSTRACT: Catalysts prepared for ethanol dehydration in a fixed-bed reactor acted as strong active acidic catalysts under reaction conditions at lower temperatures. Experimental conditions including the catalyst type [active aluminum oxide (γ-Al₂O₃) and ZSM-5 zeolite catalyst modified using two-stage through dealumination or desilication and by using the impregnation method with phosphorus and lanthanum], weight hourly space velocity (WHSV), ethanol concentration, and reaction temperature were investigated to obtain optimal reaction conditions. The catalysts were characterized using the Brunauer–Emmett–Teller method, temperature-programmed desorption of ammonia gas, thermogravimetric analysis, X-ray photoelectron spectroscopy, and X-ray diffraction. The results revealed that the ethylene yield and selectivity were 98.5 and 100%, respectively, for the ZSM-5 zeolite catalyst modified through dealumination at a temperature of 220 °C and WHSV of 2.5 h⁻¹ when the ethanol concentration was 95%. The ethylene yield and selectivity were 94.3 and 94.4%, respectively, for the ZSM-5 zeolite catalyst modified using phosphorus at a temperature of 240 °C and WHSV of 1.5 h⁻¹ when the ethanol concentration was 20%. Both of these catalysts were the most favorable among all prepared catalysts.

INTRODUCTION
Ethylene is an essential chemical in the petrochemical industry. Ethylene is traditionally produced through the steam cracking of hydrocarbons, and this method remains the predominant method in the industry. However, attention has been recently shifted toward the use of green alternatives for ethylene production to reduce greenhouse gas emissions and dependency on limited fossil fuels. Catalytic bioethanol dehydration has been primarily used as a green alternative for ethylene production. Bioethanol produced from biomass fermentation is a potential alternative feedstock instead of petroleum that is used as a chemical feedstock for ethylene production. Therefore, dehydration of ethanol to ethylene has attracted increasing attention. Bioethanol is a renewable and eco-friendly energy source that can be produced from biomass such as hemicellulose. For example, the fast-growing fern genus Pteris is not of major economic importance but is a reliable source of hemicellulose that can be converted to bioethanol.

In the catalytic dehydration of ethanol to ethylene, an acid catalyst initially protonates the hydroxyl group, which leaves as a water molecule. The conjugate base of the catalyst then deprotonates the methyl group, and the hydrocarbon rearranges into ethylene. Because this reaction is endothermic, maintaining a high reaction temperature ranging from 180 to 500 °C is essential. However, the industrial application and maintenance of such a high reaction temperature constitute a considerable portion of the energy cost because competing reactions into diethyl ether or acetaldehyde are favored outside the temperature range and thus reduce the ethylene yield. The dehydration reaction of ethanol is given as follows

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

This is the E1 reaction mechanism. In the initial studies on the dehydration of ethanol to ethylene, γ-alumina was used as a catalyst for the reaction. Because a high reaction temperature of 450 °C is required and the yield of ethylene is relatively low (80%), researchers have been focusing on modifying the catalyst to reduce the reaction temperature and increase the ethylene yield to make the reaction more economically efficient. Phillips Oel Co. (USA) uses γ-alumina treated with KOH and ZnO/Al₂O₃ for ethylene production, and Halcon SD (USA) has been using the MgO–Al₂O₃/SiO₂-based SynDol catalyst in their facilities. Bi et al. (2010) reported that the nanoscale H-ZSM-5 zeolite powder (crystal size: 50–100 nm; SiO₂/Al₂O₃ = 26) can provide a conversion rate of 98.6% and an ethylene selectivity of 99.2% at a reaction temperature of 240 °C. Moreover, the ability of H-ZSM-5 to catalyze the dehydration of ethanol to ethylene at low temperatures (200–300 °C) has made it commercially valuable and promising for further improvement in its efficiency. ZSM-5 zeolite catalysts treated by dealumination or desilication and modified with phosphorous or lanthanum have been reported. For example, Xin et al. (2014) post-treated ZSM-5 zeolite powder by desilication with sodium hydroxide, dealumination with oxalic acid, or both in a sequential way to finely tune zeolite catalysts in a hierarchical porous structure with varying acidities.

Table 1

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summarizes the ability of catalysts to dehydrate ethanol to ethylene.

Because the production concentration of the bioethanol process can reach 15−20%,3,10 we examined the ethanol feed concentration of 20−95% by using diluted industrial ethanol to simulate bioethanol. In view of saving technological energy, development of a low-temperature (<240 °C) catalyst with a high catalytic performance and stability is essential. In this study, we have developed a ZSM-5 zeolite catalyst modified using two-stage to reduce the reaction temperature and increase the ethylene selectivity and yield in ethanol dehydration.

**RESULTS AND DISCUSSION**

ZSM-5 zeolites were promising from the perspective of industrial applications, which is limited to unsatisfactory catalytic performance and low anticoking ability.8 The modification of ZSM-5 zeolites is more crucial to reduce their strong acidic sites. With regard to the coke effect, the weak acidic site has more satisfactory lifespan performance than the strong acidic site.8 The γ-Al2O3 catalyst can change its structure to increase the number of acidic sites; however, the increase in the number of acidic sites can reduce its catalytic lifespan. Moreover, the γ-Al2O3 catalyst begins to convert into other transitional phases at 500 °C.4 In this study, we first evaluated the dehydration of ethanol to ethylene by using commercial catalysts ZSM-5 (Zeolyst), Al2O3 (BASF), and γ-Al2O3/SiO2 (NKC). Ethanol conversion and ethylene selectivity were measured at different reaction temperatures. The results obtained when the feed ethanol concentration was 95% are graphically illustrated in Figure 1.

| catalyst             | Sethylene (%) | Xethanol (%) | T (°C) | LHSV/WHSV/GHSV (h⁻¹) | t (h) | refs |
|----------------------|--------------|--------------|--------|-----------------------|-------|------|
| TiO2/γ-Al2O3         | 99.4         | 100          | 360−500| 26−234b               | 400   | 4    |
| La−P-HZSM-5          | 99.9         | 100          | 240−280| 2c                    | 7     | 5    |
| nano-CAT             | 99.7         | 100          | 240    | 1e                    | 630   | 5    |
| Ag3PW12O40           | 99.2         | 100          | 220    | 6000c                 | 17    | 16   |
| TPA-MCM-41           | 99.9         | 98.0         | 300    | 2.9e                  | 17    | 18   |
| STA-MCM-41           | 99.9         | 99.0         | 250    | 2.9e                  | 19    | 19   |
| TRC-92               | 99.0         | 70.0         | 280    | 2.9e                  | 19    | 19   |
| SynDol               | 96.8         | 99.0         | 450    | 26−234d               | 4     | 4    |
| HZSM-5               | 98.6         | 98.5         | 275    | 2.37e                 | 350   | 12   |
| ZSM-5-deAl-1/25      | 100f         | 98.1         | 220    | 2.5e                  | >100  |      |
| ZSM-5-deAl-1/25      | 100f         | 96.3         | 220    | 1.5f                  | >100  |      |
| ZSM-5-deAl-1/50      | 100f         | 98.3         | 240    | 1.5f                  | 60    |      |
| ZSM-5-deAl-1/100     | 100f         | 99.8         | 240    | 1.5f                  | 50    |      |
| ZSM-5-P              | 94.4f        | 99.8         | 240    | 1.5f                  | >100  |      |
| ZSM-5-La             | 93.3f        | 97.7         | 240    | 1.5f                  | >100  |      |

**Figure 1.** Plot of (A) ethanol conversion, (B) ether yield, (C) ethylene yield, and (D) ethylene selectivity vs reaction temperature for different commercial catalysts. Ethanol(aq): 95 wt %, WHSV: 0.75 h⁻¹, catalyst: 0.4 g, and carrier gas (N2): 30 mL/min.
selectivity indicated a decreasing order for the commercial catalysts: ZSM-5 > Al₂O₃ (BASF) > γ-Al₂O₃/SiO₂ (NC). The micropore surface area (S\text{mic}) for the ZSM-5 (Zeolyst), Al₂O₃ (BASF), and γ-Al₂O₃/SiO₂ (NC) catalysts was 245, 20, and 0 m²/g, respectively.

Ethanol dehydration was incomplete, and ethanol conversion was low at lower temperatures. Furthermore, ethanol conversion for each catalyst increased with an increase in the temperature. Ethanol conversion for the γ-Al₂O₃/SiO₂ (NC) catalyst at 350 and 450 °C was 66.9 and 97.1%, respectively. The yield of the by-product (ether) exhibited a different tendency. The ether yield decreased with an increase in the temperature. As presented in Figure 1, the ethylene yield obtained using the ZSM-5 catalyst at 200 °C was 0.51%. Furthermore, 85.6% of the ethylene yield was achieved when the reaction temperature reached 280 °C. The ethylene yield obtained using the ZSM-5 catalyst was higher than that of other catalysts. In addition, ethylene selectivity exhibited the same tendency. Ethylene selectivity was low at lower temperatures because of diethyl ether production. With an increase in the temperature, ethylene selectivity increased with a concomitant decrease in the diethyl ether selectivity. The maximum ethylene selectivity for the ZSM-5, Al₂O₃ (BASF), and γ-Al₂O₃/SiO₂ (NC) catalysts was 94.7, 94.5, and 51.2% at 280, 450, and 450 °C, respectively. However, the disadvantage of the ZSM-5 catalyst was its acidity, which reduced its stability and coking resistance. In general, the ZSM-5 catalyst can be modified using desilication, dealumination, phosphorus, and lanthanum to improve its efficiency in ethanol dehydration. Thus, we modified the ZSM-5 catalyst by using four methods and studied their reactivity.

**Stability of the Catalyst in Ethanol Dehydration.**

**Effect of Time on Stream for Ethanol Concentration (95%).** The stability of the catalysts in the dehydration of ethanol to ethylene was examined under optimal reaction conditions, as listed in Table 2. Ethanol conversion and ethylene selectivity decreased with the reaction time (Figures 2 and 3). As presented in Figure 2, the ZSM-5 catalyst had poor stability. However, the ZSM-5-deAl-1/25 (220 °C), ZSM-5-La (240 °C), ZSM-5-P (240 °C), and Al₂O₃ (BASF; 350 °C) catalysts had high stability. Ethanol conversion and ethylene selectivity for all modified ZSM-5 catalysts were more than 99% after the reaction time of 100 h (Table 2). This finding demonstrates that the ZSM-5-deAl-1/25 catalyst had higher catalytic stability than the parent ZSM-5 catalyst (Figure 2). Furthermore, the ZSM-5-deAl-1/25 catalyst had higher effective catalytic activity and stability, and its ethylene yield, ethylene selectivity, and ethanol conversion did not decrease after the reaction time of 100 h.

**Effect of Time on Stream for Ethanol Concentration (20–95%).** Figure 4 presents the results of ethanol dehydration performed using the ZSM-5-deAl-1/25, ZSM-5-La, and ZSM-5-P catalysts at different ethanol feed concentrations (20–95%). The calculated ethylene conversion for ZSM-5-deAl-1/25, ZSM-5-P, and ZSM-5-La was less than 5% when the ethanol feed concentration for these three catalysts was 95% at 220 °C, 20, 60, and 95% at 240 °C, and 95% at 250 °C, respectively, and their initial ethanol conversion was 99, 95, and 95%, respectively.

**Catalytic Performance Using Commercial and ZSM-5-Modified Catalysts.** Tables 3, 4, and 5 list the effect of temperature and weight hourly space velocity (WHSV) on ethanol conversion, ethylene yield, ethylene selectivity, and space-time yield (STY) by using the ZSM-5, ZSM-5-deAl, ZSM-5-P, ZSM-5-La, and Al₂O₃ (BASF) catalysts. The catalytic activity of all catalysts became significant from 200 to 280 °C. STY is the amount of ethylene synthesized per kg of the catalyst per hour. Table 3 lists the STY for different catalysts at temperatures ranging from 220 to 280 °C. The results revealed that the ZSM-5-deAl-1/50 catalyst has higher ethanol conversion and STY when the reaction temperature was 240 and 280 °C.

The ethylene yield for the ZSM-5-deAl-1/25, ZSM-5-P, ZSM-5-La, ZSM-5-deAl-1/50, and ZSM-5-deAl-1/100 catalysts was approximately 94, 94, 91, 100, and 99%, respectively, when the reaction temperature reached 240 °C. Furthermore, the ethylene yield for ZSM-5-deAl-1/25, ZSM-5-P, and ZSM-5-La decreased to 29.8, 38.5, and 34.9%, respectively, but that for ZSM-5-deAl-1/50 and ZSM-5-deAl-1/100 increased to 100 and 100%, respectively, when the reaction temperature was increased to 280 °C. This finding indicates that the ethylene yield and selectivity for the ZSM-5-deAl-1/25, ZSM-5-P, and ZSM-5-La catalysts decreased when the reaction temperature was increased from 240 to 280 °C. This could be attributable to the increased production of by-products at a reaction temperature of 280 °C.

The dehydration of ethanol by the acidic catalysts competitively form ethane and diethyl ether. For Al₂O₃ (BASF) and ZSM-5 (Zeolyst) in Table 3, the selectivity of ethylene increases with increasing reaction temperature. High reaction temperatures are propitious to the ethylene formation via intramolecular dehydration, whereas low temperatures are favorable to diethyl ether via intermolecular dehydration. At low temperatures, not only the catalyst activity is poor but also the selectivity of ethylene is low because of a large amount of ethanol being converted to diethyl ether. The selectivity of ethylene for the other ZSM-5 modified catalysts is of the same trend, but higher temperature is decreased. The liquid hourly space velocities (LHSV) in the traditional fixed-bed reactor are as low as 0.2–0.4 h⁻¹ because of the heat transfer and intrinsic reaction rate limitations. Table 4 shows that the selectivity of ethylene is decreased when the WHSV is larger than 2.5, but the selectivity of diethyl ether behaved in the opposite way.

Ethanol conversion for the ZSM-5, ZSM-5-deAl-1/50, ZSM-5-deAl-1/100, ZSM-5-P, ZSM-5-La, and Al₂O₃ (BASF) catalysts did not improve when the reaction temperature was...
decreased to 220 °C. However, the ethylene yield for the ZSM-5-deAl-1/25 catalyst was 96.3% at a reaction temperature of 220 °C. At a low reaction temperature (220 °C), the STY for the ZSM-5-deAl-1/25 catalyst was higher than that for other catalysts. Hence, the ZSM-5-deAl-1/25 catalyst was assessed at different temperatures and WHSVs when the feed ethanol concentration was 95% (Table 4). When the reaction temperature was 240 °C and WHSV was 4.0 h⁻¹, STY was 2160 g kg⁻¹ h⁻¹, but the ethylene yield was 88.4%. When the reaction temperature was decreased to 220 °C and WHSV was 2.5 h⁻¹, the ethylene yield increased to 98.5% and STY was 1512 g kg⁻¹ h⁻¹. The ethylene yield and selectivity were 98.5 and 100%, respectively, for the ZSM-5-deAl-1/25 catalyst under optimal conditions (temperature of 220 °C and WHSV of 2.5 h⁻¹). Table S depicts the reaction performance of ethanol dehydration at a low-feed ethanol concentration (20–60%). The performance of the ZSM-5-P catalyst was excellent when the reaction temperature was 240 °C and the feed ethanol concentration was 20%. The selectivity of ethylene decreases with the decreasing concentration of ethanol in the feed, especially when the temperatures are lower than 220 °C, using ZSM-5-deAl-1/25. The selectivity of ethylene decreases with
The catalysts were characterized through temperature-programmed desorption (TPD), micropore size, and surface area analyses by using the Brunauer–Emmett–Teller (BET) method, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA).

**Crystallinity of the Catalysts.** As presented in Figure 4, the XRD patterns of the five samples exhibited well-resolved diffraction peaks that were characteristic of the mordenite framework inverted structure. The relative crystallinity was calculated according to the aggregate intensities of the three peaks at 2θ of 23.07°, 23.28°, and 23.90°. The three-peak crystallinity of the ZSM-5 zeolites were considered to be 100% crystalline. The XRD crystallinity of the ZSM-5-deAl catalyst decreased from that of the ZSM-5 peak intensity by 2θ = 23−25°.

**Figure 4.** XRD patterns of different catalysts. The values in the parenthesis show the percentage related to the parent ZSM-5 peak intensity of 2θ = 23−25°.

**Table 3.** Kinetic Data for the Dehydration of Ethanol at Ethanol(aq): 95 wt % and WHSV: 1.5 h⁻¹

| catalyst          | T (°C) | X_{ethanol} (%) | Y_{ethylene} (%) | S_{ethylene} (%) | STY (g kg⁻¹ h⁻¹) |
|-------------------|-------|-----------------|-----------------|-----------------|-----------------|
| Al₂O₃ (BASF)      | 220   | 0.335           | 7.21            | 0.13            |
| ZSM-5 (Zeolyst)   | 240   | 0.421           | 8.69            | 0.18            |
| ZSM-5-deAl-1/25   | 280   | 5.78            | 36.2            | 19.3            |
| ZSM-5-deAl-1/100  | 240   | 45.8            | 39.8            | 36.7            |
| ZSM-5-P           | 240   | 67.9            | 7.64            | 70.0            |
| ZSM-5-La          | 280   | 73.2            | 7.64            | 80.9            |
| ZSM-5-P           | 240   | 96.0            | 94.5            | 94.8            |
| ZSM-5-deAl-1/50   | 280   | 41.1            | 29.8            | 270             |
| ZSM-5-deAl-1/25   | 240   | 96.3            | 94.5            | 94.8            |
| ZSM-5-La          | 280   | 99.6            | 94.5            | 94.8            |
| ZSM-5-deAl-1/25   | 240   | 99.9            | 29.8            | 270             |
| ZSM-5-P           | 240   | 98.9            | 28.4            | 267             |
| ZSM-5-deAl-1/100  | 280   | 98.9            | 28.4            | 267             |
| ZSM-5-La          | 240   | 96.3            | 94.5            | 94.8            |
| ZSM-5-P           | 280   | 99.9            | 94.5            | 94.8            |
| ZSM-5-deAl-1/25   | 240   | 99.9            | 29.8            | 270             |
| ZSM-5-P           | 240   | 98.9            | 28.4            | 267             |
| ZSM-5-deAl-1/100  | 280   | 98.9            | 28.4            | 267             |
| ZSM-5-La          | 240   | 96.3            | 94.5            | 94.8            |
| ZSM-5-P           | 280   | 99.9            | 94.5            | 94.8            |

“X_{ethanol}: conversion of ethanol, Y_{ethylene}: yield of ethylene, and S_{ethylene}: selectivity of ethylene.”

Table 4. Kinetic Data for the Dehydration of Ethanol at Ethanol(aq): 95 wt %, WHSV: 0.75–6.0 h⁻¹, and catalyst: ZSM-5-deAl-1/25

| WHSV (h⁻¹) | T (°C) | X_{ethanol} (%) | Y_{ethylene} (%) | S_{ethylene} (%) | STY (g kg⁻¹ h⁻¹) |
|------------|-------|-----------------|-----------------|-----------------|-----------------|
| 0.75       | 220   | 94.2            | 91.8            | 97.5            | 446             |
| 240        | 97.1  | 90.2            | 92.9            | 444             |
| 280        | 98.9  | 23.5            | 23.7            | 118             |
| 1.5        | 220   | 96.3            | 96.3            | 100             | 877             |
| 240        | 99.6  | 94.5            | 94.8            | 860             |
| 280        | 99.9  | 29.8            | 29.8            | 270             |
| 2.5        | 220   | 98.1            | 98.5            | 100             | 1512            |
| 240        | 99.8  | 98.9            | 99.2            | 1512            |
| 280        | 99.8  | 31.7            | 31.8            | 479             |
| 4.0        | 220   | 94.5            | 73.4            | 77.6            | 1795            |
| 240        | 98.3  | 88.4            | 89.9            | 2160            |
| 280        | 99.6  | 35.1            | 35.2            | 859             |
| 240        | 96.2  | 65.1            | 67.7            | 1591            |
| 240        | 99.8  | 36.1            | 36.2            | 883             |

Table 5. Kinetic Data for the Dehydration of Ethanol at Ethanol(aq): 20–60 wt % and WHSV: 1.5 h⁻¹

| catalyst          | T (°C) | X_{ethanol} (%) | Y_{ethylene} (%) | S_{ethylene} (%) | STY (g kg⁻¹ h⁻¹) |
|-------------------|-------|-----------------|-----------------|-----------------|-----------------|
| ZSM-5-deAl-1/25   | 220   | 75.6            | 21.5            | 28.5            | 199             |
| (60%)             | 240   | 75.9            | 54.2            | 71.3            | 509             |
| ZSM-5-deAl-1/25   | 280   | 97.9            | 59.1            | 60.4            | 557             |
| (20%)             | 240   | 56.5            | 48.8            | 50.5            | 294             |
| ZSM-5-P           | 280   | 98.6            | 54.1            | 56.9            | 332             |
| (60%)             | 240   | 97.4            | 94.1            | 96.6            | 505             |
| ZSM-5-P           | 240   | 44.3            | 34.4            | 69.4            | 312             |
| (20%)             | 240   | 41.1            | 8.99            | 22.5            | 83.5             |
| ZSM-5-P           | 240   | 98.6            | 95.1            | 97.1            | 601             |
| (60%)             | 280   | 46.7            | 36.7            | 70.4            | 316             |
| ZSM-5-P           | 240   | 42.1            | 8.24            | 28.9            | 90.3             |
| (20%)             | 240   | 96.9            | 93.7            | 97.1            | 564             |
| ZSM-5-P           | 240   | 45.5            | 37.7            | 71.1            | 340             |
| (20%)             | 240   | 44.3            | 8.97            | 30.3            | 99.9             |
| ZSM-5-P           | 240   | 97.4            | 94.6            | 98.1            | 581             |
| (20%)             | 240   | 44.3            | 36.9            | 69.9            | 315             |
Acidic Properties of the Catalysts. NH₃-TPD was used to characterize the acidic properties of the catalysts. We observed two NH₃ desorption peaks for the ZSM-5, ZSM-5-P, ZSM-5-deSi, ZSM-5-deAl-1/25, and ZSM-5-deAl-1/100 catalysts (Figure 5). Regarding NH₃-TPD patterns, the NH₃ desorption temperature below and above 300 °C corresponded to weak and strong acidic sites, respectively. The centering of low-temperature desorption peaks at 200 °C and high-temperature desorption peaks at 400 °C was attributable to weak acidic sites and binding of NH₃ to strong acidic sites, respectively. For the five catalysts, the number of weak acidic sites was higher than that of strong acidic sites. Compared with the parent ZSM-5 catalyst, the ZSM-5 modified catalysts exhibited higher desorption temperature in the strong acidic sites, indicating that the strength of acidic sites increased by post-treatment. Upon desilication, the ZSM-5-deSi catalyst had lower number of weak and strong acidic sites than the parent ZSM-5 catalyst because the structure of the ZSM-5-deSi catalyst was destroyed (Figure 4). The desilication reaction may be conducted under relatively mild conditions to enhance the acidic sites.

Intermolecular dehydration of ethanol is a comprehensive and synergistic effect of weak and strong acidic sites. An increase in the number of weak acidic sites and in the acidity of both weak and strong acidic sites was beneficial to the catalytic activity for dehydration of ethanol to ethylene. However, strong acidity can lead to ethylene polymerization. Thus, the ZSM-5-deAl-1/25 catalyst had a high intensity and desorption temperature. Of course, except the acid strength (strong or weak), the acidity type (Brønsted or Lewis) and acid amount of both weak and strong acidic sites was bene}

Table 6. Characteristic Parameters of the Porous Structure of Fresh and Spent Catalysts

| catalyst                | surface area (m²/g) | pore volume (cm³/g) |
|-------------------------|---------------------|---------------------|
|                         | S_{micro}           | S_{meso}            | V_{micro} | V_{meso} |
| ZSM-5 (Zeolyst)         | 372 (294)           | 127 (134)           | 0.13 (0.08) | 0.13 (0.16) |
| ZSM-5-deAl-1/25-20%     | 401 (392)           | 195 (200)           | 0.11 (0.10) | 0.16 (0.16) |
| ZSM-5-deAl-1/25-60%     | 401 (385)           | 195 (194)           | 0.11 (0.10) | 0.16 (0.16) |
| ZSM-5-deAl-1/25-95%     | 401 (371)           | 195 (183)           | 0.11 (0.10) | 0.16 (0.16) |
| ZSM-5-P                 | 397 (232)           | 194 (203)           | 0.12 (0.11) | 0.19 (0.17) |
| ZSM-5-La                | 386 (195)           | 191 (165)           | 0.11 (0.09) | 0.16 (0.16) |
| ZSM-5-deSi              | 381 (282)           | 194 (144)           | 0.11 (0.07) | 0.15 (0.17) |
| Al₂O₃ (BASF)            | 197 (171)           | 20.1 (176)          | 0.01 (0.07) | 0.68 (0.56) |
| γ-Al₂O₃/SiO₂ (NKC)      | 339                 | 118 (186)           | 0.06 (0.07) | 0.30 (0.56) |

The value in the parenthesis was obtained after the reaction. BET method. t-Plot method. Barrett-Joyner-Halenda (BJH) method (adsorption branch).
catalysts. For the ZSM-5-deSi catalyst, the decrease in the amount of silicon was 7.1% and the increase in the amount of carbon was 16.6%. The desilication of the ZSM-5 catalyst resulted in a shift in the maximum of the Si 2p band to lower binding energies, indicating a decrease in the proportion of oxidized silicon groups. This behavior indicated that the desilication method made the catalyst inactive and reduced its performance.

**Coke Deposition on the Surface of the Catalyst.** TGA was performed to examine coke deposition in the Al2O3 (BASF), ZSM-5, ZSM-5-P, ZSM-5-La, and ZSM-5-deAl-1/25 catalysts after the reaction (Figure 6). The total weight loss at a temperature of 800 °C for the ZSM-5-deAl-1/25-95%, ZSM-5-deAl-1/25-20%, ZSM-5-P, ZSM-5-deAl-1/25-60%, ZSM-5, ZSM-5-La, and Al2O3 (BASF) catalysts was 2.09, 2.60, 2.86, 3.15, 3.33, 4.20, and 5.48 wt %, respectively. The weight loss below the temperature of 150 °C is attributable to physically adsorbed water in porous materials. The weight loss at temperatures of 200–800 °C is attributable to the burning of heavy coke. The amount of coke deposition for the ZSM-5 catalyst was higher than that for the ZSM-5-deAl-1/25 catalyst. This explains the reason for the high stability of the ZSM-5-deAl-1/25 catalyst.

A decrease in the S.micro and V.micro is caused by coke deposition (Table 6). The blockage of the channel by coke deposition over the spent ZSM-5 catalyst restricts the access of reactants or intermediates to the internal active sites of the catalyst. The loss of S.micro in the spent ZSM-5 and ZSM-5-deAl-1/25 catalysts was 85.2 and 18.1 m²/g, respectively. The decrease in the percentage of S.micro of the ZSM-5, ZSM-5-P, ZSM-5-La, ZSM-5-deAl-1/25, ZSM-5-deAl-1/50, and Al2O3 (BASF) catalysts was 34.7, 12.1, 28.9, 8.74, 9.35, and 100%, respectively.

A high loss of S.micro in the catalysts suggests that the coke precursors or the coke produced during the reaction procedure tends to deposit in the newly created micropores. Therefore, the newly created micropores may accommodate a part of coke deposition, consequently reducing the formation of coke deposition in its inherent micropores to some extent. We observed a reduction in the micropore blockage in the ZSM-5-deAl-1/25 zeolites. Because of the reduction in the micropore blockage in the spent ZSM-5-deAl-1/25 catalyst, most active sites were still accessible to reactants and intermediates. Therefore, ethanol conversion for the ZSM-5-deAl-1/25 catalyst was much higher than that for the ZSM-5 catalyst when the feed concentration of ethanol was 95%.

**Performance of ZSM-5-deAl.** Figure 7 presents the simulation for the dehydration of ethanol to ethylene by using ASPEN software under the following reaction conditions: 180–500 °C, ethanol feed concentration = 95%, ethanol feed rate = 0.013 mL/min, and pressure = 1 atm. The reaction formula is as follows

\[ 	ext{C}_2	ext{H}_5	ext{OH} \rightarrow 	ext{C}_2	ext{H}_4 + 	ext{H}_2	ext{O} \]  

\[ 2	ext{C}_2	ext{H}_5	ext{OH} \rightarrow 	ext{C}_2	ext{H}_5	ext{OC}_2	ext{H}_5 + 	ext{H}_2	ext{O} \]

The simulation for the dehydration of ethanol indicates that ethanol conversion decreased below 220 °C. By comparing the simulation results with this study results, we observed that the aforementioned conditions are optimal for ethanol dehydration.

**CONCLUSIONS**

The modification of the ZSM-5 catalyst by using the dealumination method improved its catalytic performance and anticoking ability for the dehydration of ethanol to ethylene at a low temperature, which could be attributable to the tuned acidic sites, pore structure, and synergistic interaction with aluminum. The ZSM-5-deAl-1/25 and ZSM-5-P catalysts restricted the formation of coke, which can lead to the activation of the catalysts, and an increase in the stability of the catalysts.

**Table 7. Mass Surface Concentration (%) Obtained Using XPS Analysis**

| catalyst                  | C 1s (%) | O 1s (%) | Si 2p (%) | Al 2p (%) | P 2p (%) | La 3d (%) | Na 1s (%) |
|---------------------------|----------|----------|-----------|-----------|----------|-----------|-----------|
| ZSM-5 (Zeolyst)           | 13.6     | 51.9     | 34.4      | 0.1       | 0.37     |           |           |
| ZSM-5-deSi                | 30.2     | 42.1     | 27.3      | 0.03      | 0.1      |           |           |
| ZSM-5-P                   | 21.8     | 46.5     | 31.6      | 0.08      | 0.02     | 0.01      |           |
| ZSM-5-La                  | 19.7     | 47.4     | 32.8      | 0.09      | 0.1      |           |           |
| ZSM-5-deAl-1/25           | 26.3     | 44.4     | 29.2      | 0.1       |          |           |           |
| ZSM-5-deAl-1/100          | 23.7     | 45.8     | 30.4      | 0.1       |          |           |           |

**Figure 6.** TGA curves of used catalysts: BASF, ZSM-5, ZSM-5-P, ZSM-5-La, and ZSM-5-deAl-1/25 under 20–95 wt % feedstock/100 h.

**Figure 7.** Simulation plot of ethanol conversion and product yield on reaction temperature in ethanol dehydration using ASPEN software. The solid line (——) is the result obtained with the ZSM-5-deAl-1/25 catalyst; WHSV = 2.5 h⁻¹ and ethanol feed concentration = 95%.
catalysts. The most favorable ethylene yield and selectivity (98.5 and 100%, respectively) for the ZSM-5-deAl-1/25 catalyst were obtained at a WHSV of 2.5 h⁻¹, lifespan reaction time of 100 h, reaction temperature of 220 °C, and ethanol feed concentration of 95% and for the ZSM-5-P catalyst at a lifespan reaction time of 100 h, WHSV of 1.5 h⁻¹, reaction temperature of 240 °C, and ethanol feed concentration of 20%. The mesoporous structure of the catalyst and a strong acidic site (high temperature in NH3TCD) can enhance the catalytic stability and ethylene selectivity.

### EXPERIMENTAL SECTION

**Materials.** We purchased zeolite ammonium ZSM-5 (CBV28014, SiO₂/Al₂O₃ mole ratio = 280, surface area = 400 m²/g, and cation form = ammonium) from Zeolyst International (Valley Forge, USA), ethanol (95%) from Echo Chemical (Miaoli, Taiwan), ammonium phosphate and aluminum nitrate-9-hydrate (99%) from J.T. Baker (Mexico, USA), ammonium nitrate and lanthanum nitrate hexahydrate from Sigma (Utah, USA), and ethylene (99%) from Ming Yang (Taoyuan, Taiwan). The reagents were used as supplied by the manufacturer.

**Preparation of the Catalyst.** Preparation of the ZSM-5-deSi Catalyst. We performed the desilication treatment of the ZSM-5 catalyst (3.3 g) by vigorously stirring it in 100 mL of aqueous NaOH (0.2 M) solution in a flask at 65 °C for 30 min, followed by filtration and thorough washing with deionized (DI) water. The solid sample was isolated and dried at 100 °C for 24 h in an oven. Then, we mixed the sample (1 g) in 30 mL of NH₄NO₃ (1 M) solution and stirred it vigorously. We placed the sample in a boat quartz tube and then subsequently calcined it in static air from room temperature to 550 °C (ramp rate of 1 °C/min). After calcination, we placed the catalyst in a sample bottle and maintained the bottle at room temperature.

Preparation of the ZSM-5-deAl Catalyst Modified Using Two-Stage. First stage: the dealumination treatment of the ZSM-5 catalyst (1.0 g) was carried out in 50 mL of aqueous oxalic acid (0.5 M) solution in a flask and then heated to 120 °C for 2 h. The solid product was filtered and dried at 100 °C for 24 h in an oven. Second stage: then, we mixed 1 g of the filtered sample in 25, 50, and 100 mL of oxalic acid solution (0.5 M) separately, vigorously stirred it, and named them ZSM-5-deAl-1/25, ZSM-5-deAl-1/50, and ZSM-5-deAl-1/100, respectively. Furthermore, we calcined these samples in static air from room temperature to 550 °C (ramp rate of 1 °C/min).

**Preparation of the Phosphorous- and Lanthanum-Modified Catalyst.** The phosphorous (ZSM-5-P) or lanthanum (ZSM-5-La) treatment of the ZSM-5 catalyst (1 g) was performed by suspending the catalyst in 50 mL of DI water and then adding the desired volume (100 mL, 1 wt %) of aqueous (NH₄)₃HPO₄ or La(NO₃)₃·6H₂O (0.02 M) solution, respectively. After agitation at 60 °C for 6 h, the excess water was removed under reduced pressure. The residue was dried at 60 °C in an oven and then calcined at 500 °C for 6 h.

**Activity of Ethanol Dehydration.** Figure 8 presents the schematic of the experimental apparatus. The dehydration reaction was performed in a fixed-bed reactor. First, 0.4 g of 60–80-mesh catalyst particles was added in a U-type quartz tube (diameter, 1 cm and length, 24 cm) isolated by silicon carbide cotton and then placed in an electrically heated furnace. The temperature was controlled using a microprocessor-based temperature controller through a K-type thermocouple (Maxthermo, MC-2438, Taiwan). Ethanol (20, 60, or 95%) was injected into the reactor by using a liquid pump (LC-10A, Shimadzu, Japan) under a nitrogen carrier gas flow rate of 30 mL/min. The WHSV of ethanol was set at a selected value (0.75–6.0 h⁻¹).

Ethanol and the condensate from the condenser (Figure 8H) were determined using a gas chromatography–flame ionization detector (GC–FID; GC2014, Shimadzu, Japan) equipped with a column of 7HK-G013-22 ZB-WAX (length, 30 m; i.d., 0.53 mm; and film, 1 μm; Zebra, Los Angeles, USA) under nitrogen carrier gas (30 mL/min). The oven temperature was set at 50–100 °C (ramp rate of 10 °C/min). The sample was withdrawn at a time interval of 1 h. C₂H₄ and (C₂H₅)₂O obtained from the dilute tube (Figure 8J) were determined using a GC–FID (GC14B, Shimadzu, Japan) equipped with a column of Porapak-Q-141023J (length, 3 m and i.d., 2 mm; Quadrex, Bethany, USA) under a nitrogen carrier gas flow rate of 30 mL/min. The oven temperature was set at 180 °C. The sample was withdrawn at a time interval of 1 h.

**Calculation of the Conversion and Yield of Ethylene and Ether.** WHSV is defined as the ratio of the hourly feed flow rate of ethanol and water mixture to the catalyst weight. The ethanol conversion (X_\text{ethanol}), ethylene selectivity (S_\text{ethylene}), ether yield (Y_\text{ether}), and ethylene yield (Y_\text{ethylene}) are defined as follows.
$X_{\text{ethanol}} = \left( \frac{M_{\text{e0}} - M_{\text{e1}}}{M_{\text{e0}}} \right) \times 100\%$

(4)

$Y_{\text{ether}} = \left( \frac{M_{\text{e2}}}{M_{\text{e0}}} \right) \times 100\%$

(5)

$S_{\text{ethylene}} = \left( \frac{M_{\text{e1}}}{M_{\text{e0}} - M_{\text{e1}}} \right) \times 100\%$

(6)

$Y_{\text{ethylene}} = \left( \frac{M_{\text{e1}}}{M_{\text{e0}}} \right) \times 100\%$

(7)

where $M_{\text{e0}}, M_{\text{e1}}, M_{\text{e2}}$ are the molar amounts of ethanol after the reaction, ethanol before the reaction, and ethene after the reaction, respectively.

Characterization of the Catalytic Property. The acidity and distribution were analyzed through ammonia (NH$_3$) adsorption and TPD of NH$_3$ gas (NH$_3$-TPD; Micromeritics, AutoChem 2950 HP, USA). We heated 0.1 g of the catalyst sample for 1 h at 500 °C under a helium flow rate of 40 mL/min and then held it at 100 °C for impulse NH$_3$ adsorption. When the saturated adsorption was achieved, the system was swept with helium for 15 min. Then, the temperature was programmed to increase from 700 °C at a ramp rate of 10 °C/min. Nitrogen adsorption–desorption isotherm was measured at −196 °C on ASAP 2020 (Micromeritics, USA). Before measurement, the sample was degassed in vacuum at 200 °C for 200 min (ramp rate of 10 °C/min). The BET method was used to calculate the specific surface area by using the adsorption data in a relative pressure ranging from 0.02 to 0.25. XRD patterns were recorded on a D/Max-2500 X-ray diffractometer (Shimadzu Labx XRD-6000, Japan) with Cu Kα radiation by using 0.1 g of the catalyst and instrumental settings of 40 kV and 40 mA. The scanning range was from 10° to 90° at a ramp rate of 10°/min. The surface chemistry of the samples was analyzed through XPS. The XPS analyses of the samples were obtained using a 5700C model Physical Electronics apparatus (PerkinElmer, USA) with Mg Kα radiation (1253.6 eV) by using 0.1 g of the catalyst. The XPS peaks were fitted using least squares with Gaussian–Lorentzian peak shapes. The thermal property of the samples after the reaction was measured using TGA (TA Instruments Q50, USA) to monitor the amount of coke deposition. The samples were heated from room temperature to 800 °C at a ramp rate of 10 °C/min under a nitrogen flow. For the FTIR analysis, approximately 25 mg of the sample and 1 g of KBr were weighed, milled, and ground in an agate mortar, until a fine powder with a uniform particle size was obtained. It was then pressed with a steel die to obtain a thin wafer. The wafers of fresh and used catalysts were activated in situ in an infrared cell under vacuum (10$^{-6}$ mbar) at 623 K (fresh sample) and 423 K (coked samples) for 2 h and then cooled to room temperature. After the saturated adsorption of pyridine at room temperature, the sample was desorbed under vacuum at 423, 573, and 723 K. The FTIR spectra were recorded in the transmission mode with a resolution of 4 cm$^{-1}$.

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Notes

The authors declare no competing financial interest.

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