Ethylene Production from Ethanol Dehydration over Zeolite Y under Mild Conditions

Jiah Chee Soh, Soo Ling Chong and Chin Kui Cheng

Abstract—The production of ethylene via catalytic ethanol dehydration was investigated over commercial zeolite Y in a fixed bed reactor at mild operation temperature (573 and 623 K) and ethanol pressure of 33 kPa. The reaction results indicated that zeolite Y has higher ethanol conversion at 623 K. H-Y (80) demonstrated the highest ethanol conversion of 71.41% and selectivity towards ethylene of 91.84% was achieved at 623 K.

Keywords—dehydration, ethanol, ethylene, zeolite Y

I. INTRODUCTION

Ethylene is one of the most commonly used monomer in synthesizing polyethylene. Conventionally, ethylene is often produced via thermal steam cracking using petroleum or natural gas feedstocks. However, CO2 emission has become a crucial issue in the petrochemical industry. Thus, catalytic ethanol dehydration may utilize ethanol instead of petroleum, which can reduce CO2 emission, at the same time synthesize ethylene, which is a significant chemical in the polymer manufacturing industry.

For catalytic ethanol dehydration, there are two parallel pathways that can occur:

\[ \text{C}_2\text{H}_5\text{OH} \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad +44.9 \text{kJ/mol} \quad (1) \]

\[ 2\text{C}_2\text{H}_5\text{OH} \leftrightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O} \quad -25.1 \text{kJ/mol} \quad (2) \]

The main reaction and side reaction are endothermic and exothermic respectively. Thus, high reaction temperature favours the formation of ethylene, while low reaction temperature is preferable for the formation of diethyl ether.

To fully utilize ethanol as the feedstock for ethylene synthesis, the development of potential catalysts is the crucial step. In dehydration of ethanol, catalysts such as alumina [1–3], silicoaluminophosphates (SAPO) [4,5], H-ZSM-5 [6–8], titania and zirconia [9], magnesium oxides [10], manganese oxides [11], calcium oxides, tungstophosphoric acid [12], and lanthanum phosphates [13] have been employed in the study.

Previous research found that Lewis acid sites are more selective for ethylene production [14], thus, dopants that have been studied are mostly acidic in nature. H-ZSM-5 was modified by phosphoric acid and become highly active and selective towards ethylene at 673 K and become extremely stable for more than 200 h [7]. Besides that, lanthanum phosphorus modified H-ZSM-5 can achieve almost total ethylene selectivity with excellent ethanol conversion [15]. However, there has been no report on the usage of wide range Si/Al ratio of zeolites Y for ethanol dehydration so far. In continuation of our study for using zeolites Y [16] as an alternative ethylene synthesis route, we report herein that mild reaction temperatures can show promising catalytic performance in ethanol dehydration.

II. EXPERIMENTAL

A. Catalysts

The commercial lower range zeolite Y (Si/Al = 5.1:1 and 12:1) were purchased from Alfa Aesar, United States of America while higher range zeolite Y (Si/Al = 30:1, 60:1 and 80:1) catalysts were procured from Zeolyst, United States of America. Meanwhile absolute ethanol was purchased from Merck, United States of America. Distilled water from Aqua Matic AEC/8S was obtained readily from the laboratory of Universiti Malaysia Pahang.

B. Catalysts Characterization

The commercial zeolite Y was used as received. The characterization of fresh zeolite Y which includes N2 physisorption, ammonia temperature programmed desorption (NH3-TPD), thermogravimetric analysis (TGA), scanning electron microscopy with X-ray analysis (SEM-EDX), Fourier transform infrared (FTIR) and X-ray diffraction (XRD) has been reported and discussed in previous publication [16].

C. Reaction Studies

The ethanol dehydration activity evaluation was carried out in a fixed bed reactor. A stainless cylindrical tube with outer diameter (OD) 9.525 mm (0.375”) and length of 410 mm (16.14”) was constructed. For each run, 0.3 g of catalyst was sandwiched between quartz wool at the centre of the tube and the reaction temperature was detected and accurately controlled by a 1/16” K-type thermocouple placed at the centre of furnace wall. Ethanol partial pressure was set at 33 kPa and the reaction temperature (573 K, and 623 K) was...
manipulated to study the conversion of ethanol and selectivity of ethylene. The Alicat MC Series electronic mass flow controller was used to regulate the flow (hence the partial pressure) of diluent gas, N2, while Lab Alliance Series 1 HPLC pump was used to regulate the partial pressure or liquid flow rates of ethanol at the inlet. The gaseous products were collected and identified using Shimadzu GC-2011 furnished with a thermal conductivity detector for detecting C2H4 and other hydrocarbons. Rtx®-1, Rt®-Q-BOND and RT®-MSIEVE-5A were used as the columns and Helium was used as the carrier gas at a flow rate 20 ml min-1 STP, and the column and detector temperatures were set at 353 K and 473 K, respectively. The ethanol conversion (\( \chi \)) and selectivity to ethylene (\( S \)) were calculated as shown in the formula:

\[
\chi_{C_2H_5OH}(\%) = \frac{2x_{C_2H_4} + \sum_{i=1}^{6} i \times F_i}{2x_{C_2H_5OH}} \times 100\% \quad (3)
\]

\[
S_{C_2H_4}(\%) = \frac{F_{C_2H_4}}{F_T} \times 100\% \quad (4)
\]

where \( F_{C_2H_4} \) and \( F_T = \sum_{i=1}^{6} i \times F_i \) represent the flow rate of components.

### III. Results and Discussion

**A. Catalysts**

Table 1 listed some data of the zeolite Y catalysts used in this study. The data is made available by the manufacturers of the commercial catalysts.

**TABLE 1: TEXTURAL PROPERTIES OF ZEOLITE Y**

<table>
<thead>
<tr>
<th>Notation</th>
<th>Commercial name</th>
<th>Manufacturer</th>
<th>SiO(_2)/Al(_2)O(_3)</th>
<th>Surface area (m(^2) \text{g}^{-1})</th>
<th>Na (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Y (5)</td>
<td>-</td>
<td>Alfa Aesar</td>
<td>5.1</td>
<td>925</td>
<td>-</td>
</tr>
<tr>
<td>NH(_2)-Y (12)</td>
<td>-</td>
<td>Alfa Aesar</td>
<td>12</td>
<td>750</td>
<td>-</td>
</tr>
<tr>
<td>H-Y (30)</td>
<td>CBV 720</td>
<td>Zeolyst</td>
<td>30</td>
<td>780</td>
<td>0.03</td>
</tr>
<tr>
<td>H-Y (60)</td>
<td>CBV 760</td>
<td>Zeolyst</td>
<td>60</td>
<td>720</td>
<td>0.03</td>
</tr>
<tr>
<td>H-Y (80)</td>
<td>CBV 780</td>
<td>Zeolyst</td>
<td>80</td>
<td>780</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*Data from manufacturers

**TABLE II: AVERAGE ETHANOL CONVERSION AND ETHYLENE SELECTIVITY OF ZEOLITE Y CATALYSTS**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>573 K</th>
<th>623 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (%)</td>
<td>Selectivity (%)</td>
<td>Conversion (%)</td>
</tr>
<tr>
<td>NH(_2)-Y (5)</td>
<td>27.21</td>
<td>83.50</td>
</tr>
<tr>
<td>NH(_2)-Y (12)</td>
<td>0.41</td>
<td>13.39</td>
</tr>
<tr>
<td>H-Y (30)</td>
<td>31.09</td>
<td>59.04</td>
</tr>
<tr>
<td>H-Y (60)</td>
<td>50.77</td>
<td>89.50</td>
</tr>
<tr>
<td>H-Y (80)</td>
<td>48.46</td>
<td>48.79</td>
</tr>
</tbody>
</table>

From Fig. 2 and 3, the ethanol conversion and ethylene selectivity of zeolite Y catalysts in ethanol dehydration showed a consistent and stable trend with no drastic decrease or increase in the activity. In the 1 h reaction, zeolite Y catalysts consistently showed a higher catalytic reactivity at 623 K compared to 573 K. The process of dehydration of ethanol is endothermic, thus higher reaction temperature is more preferable for zeolite Y to catalyze this reaction. Besides...
That, the results also supported by previous study whereby ethanol dehydration is a comprehensive and synergistic effect of weak and strong acid sites, whereby the amount of weak acid sites are particularly helpful in ethanol dehydration [5]. Thus, H-Y (80) with high Si/Al ratio and sufficient strength of weak and moderately strong acid sites can achieve high ethanol conversion with excellent selectivity towards ethylene.

**IV. CONCLUSION**

From the results, it can be summarized that mild reaction temperature can produce ethylene, but higher reaction temperature is more favorable for ethylene formation. Besides that, high Si/Al ratio and surface area also can enhance the catalytic performance of zeolite Y catalysts. Thus, H-Y (80) with highest Si/Al ratio displayed the best catalytic performance with more than 90% of ethylene selectivity at temperature 623 K. Hence, the catalytic performance of zeolites Y in terms of both conversion of ethanol and selectivity to ethylene increase in order of Si/Al ratio 12:1 < 5.1:1 < 30:1 < 60:1 < 80:1.

**ACKNOWLEDGMENT**

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**REFERENCES**


