

# Ethylene Production from Ethanol Dehydration over Zeolite Y under Mild Conditions

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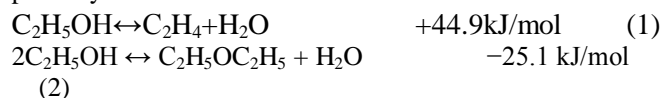
**Abstract**—The production of ethylene via catalytic ethanol dehydration was investigated over commercial zeolite Y in a fixed bed reactor at mild operation temperature (573 and 623 K) and ethanol pressure of 33 kPa. The reaction results indicated that zeolite Y has higher ethanol conversion at 623 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, CO<sub>2</sub> emission has become a crucial issue in the petrochemical industry. Thus, catalytic ethanol dehydration may utilize ethanol instead of petroleum, which can reduce CO<sub>2</sub> 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:



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 N<sub>2</sub> physisorption, ammonia temperature programmed desorption (NH<sub>3</sub>-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, N<sub>2</sub>, 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 C<sub>2</sub>H<sub>4</sub> 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<sup>-1</sup> STP, and the column and detector temperatures were set at 353 K and 473 K, respectively. The ethanol conversion ( ) and selectivity to ethylene ( ) were calculated as shown in the formula:

$$X_{C_2H_5OH}(\%) = \frac{2 \times F_{C_2H_4} + \sum_{i=1-6} i \times F_{C_i}}{2 \times F_{C_2H_5OH}} \times 100\% \quad (3)$$

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

where  $F_{C_2H_4}$ ,  $F_{C_2H_5OH}$  and  $F_T = \sum_{i=1-6} i \times F_{C_i}$  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

Notation	Commercial name	Manufacturer	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mol ratio	Surface area (m <sup>2</sup> g <sup>-1</sup> )*	Na (%)*
H <sub>3</sub> -Y (5)	-	Alfa Aesar	5.1	925	-
NH <sub>3</sub> -Y (12)	-	Alfa Aesar	12	730	-
H-Y (30)	CBV 720	Zeolyst	30	780	0.03
H-Y (60)	CBV 760	Zeolyst	60	720	0.03
H-Y (80)	CBV 780	Zeolyst	80	780	0.03

\*Data from manufacturers

#### B. Reaction Studies

The ethanol conversion and ethylene selectivity over commercial zeolite Y are displayed in Table 2, while the catalytic performance based on 1 h reaction time on stream is shown in Fig. 2 and 3. Overall, mild reaction temperature can produce significant amount of ethylene. From Table 2, it can be observed that the catalysts activity is higher at 623 K.

NH<sub>3</sub>-Y (5) consistently showed high ethylene selectivity (> 80.0%) even at 573 K, but the ethanol conversion is relatively low compared to other zeolite Y catalysts. NH<sub>3</sub>-Y (12) has the lowest ethanol conversion (0.41%) and ethylene selectivity (13.39%) at both reaction temperatures. This is because Si/Al ratio plays an important role in ethanol dehydration. Ethylene tends to form in the surroundings with silica like-structure [14]. Thus, NH<sub>3</sub>-Y (12) with low Si/Al ratio and low surface area demonstrated poorest catalytic activity. The carrier ion (NH<sub>3</sub><sup>+</sup>) of NH<sub>3</sub>-Y (5) and NH<sub>3</sub>-Y (12) does not contribute to the low catalytic performance of the catalysts because high reaction temperature or calcinations of ammonium type zeolite will convert the ammonium ion to hydrogen ion [17]. Hence, in the reaction, both catalysts are eventually been converted into H<sup>+</sup> form of zeolite Y. Meanwhile both H-Y (30) and H-Y (60) displayed almost similar catalytic performance with ethanol conversion and ethylene selectivity of ~ 50% and ~ 90% respectively at 623 K. Among all the tested zeolite Y catalysts, H-Y (80) with the highest Si/Al ratio (80:1) achieved the highest conversion of 71.41% and ethylene selectivity of 91.84% at 623 K. According to previous study based on its physicochemical properties, H-Y (80) consisted of high number of weak and moderately strong acid sites, which is favored for the production of ethylene [16].

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

Catalysts	573 K		623 K	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
NH <sub>3</sub> -Y (5)	27.21	83.50	22.28	84.07
NH <sub>3</sub> -Y (12)	0.41	13.39	0.88	18.91
H-Y (30)	31.09	59.04	53.11	90.89
H-Y (60)	50.77	89.50	49.85	90.08
H-Y (80)	48.46	48.79	71.41	91.84

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

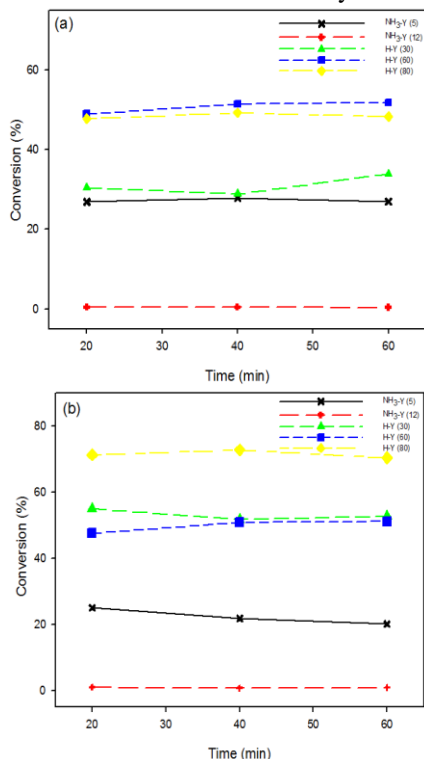


Fig. 1: Ethanol conversion over zeolite Y at reaction temperatures of (a) 573 K and (b) 623 K; ethanol partial pressure of 33 kPa for 1 h time on stream reaction.

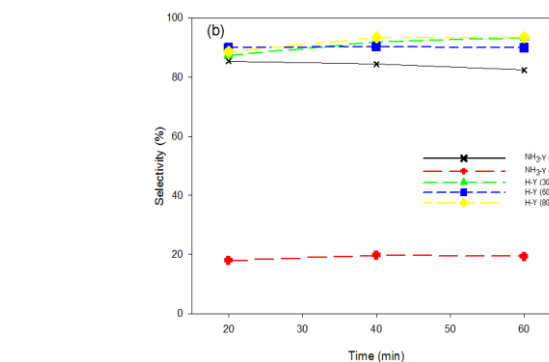
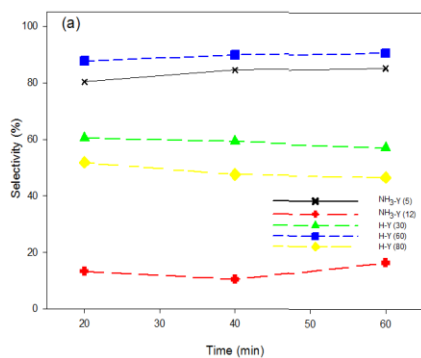


Fig. 2: Ethylene selectivity over zeolite Y at reaction temperatures of (a) 573 K and (b) 623 K; ethanol partial pressure of 33 kPa for 1 h time on stream reaction

#### 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

This work is supported by Universiti Malaysia Pahang Short Term Grant RDU160335. We also like to express our gratitude to Assoc. Prof. Ir. Dr. Chin Sim Yee for providing us with the free zeolite Y catalyst sample.

#### REFERENCES

- [1] T.K. Phung, L. Proietti Hernández, A. Lagazzo, G. Busca, Dehydration of ethanol over zeolites, silica alumina and alumina: Lewis acidity, Brønsted acidity and confinement effects, *Appl. Catal. A Gen.* 493 (2015) 77–89. doi:10.1016/j.apcata.2014.12.047. <https://doi.org/10.1016/j.apcata.2014.12.047>
- [2] S. Hajimirzaee, M. Ainte, B. Soltani, R.M. Behbahani, G.A. Leeke, J. Wood, Dehydration of methanol to light olefins upon zeolite / alumina catalysts : Effect of reaction conditions , catalyst support and zeolite, *Chem. Eng. Res. Des.* xxx (2014) xxx–xxx. doi:10.1016/j.cherd.2014.05.011. <https://doi.org/10.1016/j.cherd.2014.05.011>
- [3] T.K. Phung, A. Lagazzo, M.Á. Rivero Crespo, V. Sánchez Escribano, G. Busca, A study of commercial transition aluminas and of their catalytic activity in the dehydration of ethanol, *J. Catal.* 311 (2014) 102–113. doi:10.1016/j.jcat.2013.11.010. <https://doi.org/10.1016/j.jcat.2013.11.010>
- [4] U. Chinniyomphanich, P. Wongwanichsin, S. Jitkarnka, SnxOy/SAPO-34 as catalysts for catalytic dehydration of bio-ethanol: impacts of oxidation state, interaction, and loading amount, *J. Clean. Prod.* 111 (2016) 25–33. doi:10.1016/j.jclepro.2015.09.069. <https://doi.org/10.1016/j.jclepro.2015.09.069>
- [5] Y. Chen, Y. Wu, L. Tao, B. Dai, M. Yang, Z. Chen, X. Zhu, Dehydration reaction of bio-ethanol to ethylene over modified SAPO catalysts, *J. Ind. Eng. Chem.* 16 (2010) 717–722. doi:10.1016/j.jiec.2010.07.013. <https://doi.org/10.1016/j.jiec.2010.07.013>
- [6] C.B. Phillips, R. Datta, Production of Ethylene from Hydrous Ethanol on H-ZSM-5 under Mild Conditions, *J. Am. Chem. Soc.* 36 (1997) 239–244. doi:10.1021/ie9702542.

- <https://doi.org/10.1021/ie9702542>
- [7] K. Ramesh, C. Jie, Y.F. Han, A. Borgna, Synthesis, characterization, and catalytic activity of phosphorus modified H-ZSM-5 catalysts in selective ethanol dehydration, *Ind. Eng. Chem. Res.* 49 (2010) 4080–4090. doi:10.1021/ie901666f.  
<https://doi.org/10.1021/ie901666f>
- [8] D. Däumer, M. Seifert, W. Reschetilowski, Durability improvements of H-ZSM-5 zeolite for ethanol conversion after treatment with chelating agents, *Microporous Mesoporous Mater.* 219 (2016) 66–76. doi:10.1016/j.micromeso.2015.07.031.  
<https://doi.org/10.1016/j.micromeso.2015.07.031>
- [9] T.K. Phung, L. Proietti Hernández, G. Busca, Conversion of ethanol over transition metal oxide catalysts: Effect of tungsta addition on catalytic behaviour of titania and zirconia, *Appl. Catal. A Gen.* 489 (2015) 180–187. doi:10.1016/j.apcata.2014.10.025.  
<https://doi.org/10.1016/j.apcata.2014.10.025>
- [10] T.W. Elkins, H.E. Hagelin-Weaver, Characterization of Mn–Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> and Mn–Na<sub>2</sub>WO<sub>4</sub>/MgO catalysts for the oxidative coupling of methane, *Appl. Catal. A Gen.* 497 (2015) 96–106. doi:10.1016/j.apcata.2015.02.040.  
<https://doi.org/10.1016/j.apcata.2015.02.040>
- [11] M. Doheim, Catalytic conversion of ethanol and isopropanol over the Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system doped with Na<sub>2</sub>O, *Mater. Lett.* 55 (2002) 304–311. doi:10.1016/S0167-577X(02)00383-X.  
[https://doi.org/10.1016/S0167-577X\(02\)00383-X](https://doi.org/10.1016/S0167-577X(02)00383-X)
- [12] P. Vázquez, L. Pizzio, C. Cáceres, M. Blanco, H. Thomas, E. Alesso, L. Finkielstein, B. Lantaño, G. Moltrasio, J. Aguirre, Silica-supported heteropolyacids as catalysts in alcohol dehydration reactions, *J. Mol. Catal. A Chem.* 161 (2000) 223–232. doi:10.1016/S1381-1169(00)00346-0.  
[https://doi.org/10.1016/S1381-1169\(00\)00346-0](https://doi.org/10.1016/S1381-1169(00)00346-0)
- [13] T.T.N. Nguyen, V. Ruaux, L. Massin, C. Lorentz, P. Afanasiev, F. Maugé, V. Bellière-Baca, P. Rey, J.M.M. Millet, Synthesis, characterization and study of lanthanum phosphates as light alcohols dehydration catalysts, *Appl. Catal. B Environ.* 166–167 (2015) 432–444. doi:http://dx.doi.org/10.1016/j.apcatb.2014.12.004.  
<https://doi.org/10.1016/j.apcatb.2014.12.004>
- [14] T.K. Phung, G. Busca, Ethanol dehydration on silica-aluminas: Active sites and ethylene/diethyl ether selectivities, *Catal. Commun.* 68 (2015) 110–115. doi:10.1016/j.catcom.2015.05.009.  
<https://doi.org/10.1016/j.catcom.2015.05.009>
- [15] N. Zhan, Y. Hu, H. Li, D. Yu, Y. Han, H. Huang, Lanthanum-phosphorous modified HZSM-5 catalysts in dehydration of ethanol to ethylene: A comparative analysis, *Catal. Commun.* 11 (2010) 633–637. doi:10.1016/j.catcom.2010.01.011.  
<https://doi.org/10.1016/j.catcom.2010.01.011>
- [16] J.C. Soh, S.L. Chong, S.Y. Chin, C.K. Cheng, Catalytic performance of commercial Zeolites Y as catalyst for ethylene production from ethanol dehydration, *Malaysian J. Catal.* 2 (2017) 1–7.
- [17] J.J.F. Saceda, K. Rintramee, S. Khabuanchalad, S. Prayoonpokarach, R.L. de Leon, J. Wittayakun, Properties of zeolite Y in various forms and utilization as catalysts or supports for cerium oxide in ethanol oxidation, *J. Ind. Eng. Chem.* 18 (2012) 420–424. doi:10.1016/j.jiec.2011.11.108.  
<https://doi.org/10.1016/j.jiec.2011.11.108>