The Influence of Propan-1-Ol on Performance of Alumina-Silica Catalyst over Ethanol Dehydration

Sasiradee Jantasee, Prajak Kanya, Wasuwat Ngoksilapa, and Bunjerd Jongsomjit

Abstract—This research investigated the effect of propan-1-ol on a performance of ethanol dehydration by using an alumina-silica composite (Al_2O_3-SiO_2) catalyst. It was compared the results to a H-Beta zeolite catalyst. Alumina-silica composite catalyst was prepared in the ratio of 60:40 by precipitation method. The catalysts were characterized using various techniques. The catalysts were tested catalytic activity over the dehydration of ethanol mixed with propan-1-ol at 1 atm of total pressure and the temperature range between 200 to 400 °C. The results show that propan-1-ol decreased ethanol conversion and ethylene yield of the Al_2O_3-SiO_2 catalyst about 50% compared to the dehydration of pure ethanol over the same catalyst. Nevertheless, propan-1-ol did not significantly affect the ethylene selectivity of this catalyst. Ethanol to ethylene preferable occurred at high temperature but propan-1-ol to propylene preferable occurred at low temperature.

Index Terms—Ethanol dehydration, alumina-silica, zeolite, propan-1-ol.

I. INTRODUCTION

Decreasing amount of petroleum feedstocks and problem with greenhouse gases result in high attention to a biomass utilization [1], [2]. Recently, ethanol utilization is an important alternative to produce fuels for motor vehicle, hydrogen, or chemicals such as ethylene, acetaldehyde, and diethyl ether [3]-[6]. This is because ethanol can be produce from renewable sources. Moreover, biomass-derived ethanol can reduce carbon dioxide emissions [1]. The chemicals production from an ethanol can decrease operating temperature and reduce energy consumption compared to the production from petroleum feedstocks. However, the chemicals production from an ethanol should be able to generate as much chemicals as from petroleum feedstocks. Ethanol dehydration is one of the interesting processes which has been widely studied in academia and industry [7]-[9]. Converting ethanol to ethylene or other chemicals can be obtained by catalytic dehydration using solid acid catalysts such as alumina, zeolite, silica, alumina-silica and mixed metal oxide (such as titanium oxides, cobalt oxides,

chromium oxide and silver salt of tungstophosphoric acid) [10]-[14].

Many research commonly studied the use of pure ethanol as a feedstock for ethanol dehydration and few research have been investigated on the dehydration of a mixture of water and pure ethanol [8], [10]-[14]. The use of a low purity of ethanol produced by simple flash distillation or a crude bioethanol limiting the purification processes may result in a lower production cost of ethanol dehydration compared to that of a pure ethanol. The dehydration of low purity of ethanol differs from that of pure ethanol because many impurities may affect the catalyst performance. Other alcohols are the most prevailing impurities in crude bioethanol [15], [16]. Propan-1-ol is one of major impurities in crude bioethanol [16].

In this study, propan-1-ol was selected as model to test the performance of catalysts over the dehydration of ethanol containing impurity. The catalytic performance of alumina-silica (Al_2O_3-SiO_2) and H-Beta zeolite catalysts were compared for the dehydration of ethanol with propan-1-ol as model impurities.

II. MATERIALS AND EXPERIMENTAL

A. Materials

Tetraethyl orthosilicate (TEOS, 98%), Cetyltrimethylammonium bromide (CTAB, 98%), Aluminium nitrate (98%), and ammonia 30% were purchased from Sigma-Aldrish. H-beta zeolite was supplied from TOSOH which was calcined in air at 700 °C for 6 h before use. Ethanol (95%), 1-propanol (95%) were used for a reaction test purchased from Merck and Sigma-Aldrich, respectively. Ultra-high purity grade nitrogen was supplied from Linde.

B. Preparation of Alumina-Silica Catalyst

The desired amount of ammonia solution was mixed with 3.3 g of cetyltrimethylammonium bromide, and then stirred for 30 min. After that 6.3 g of tetraethyl orthosilicate was added into the mixture and stirred for 1 h. Then, 16.89 g of aluminium nitrate was filled into the mixture, and then stirred for 1 h. The resulting product was filtrated, dried at room temperature for 12 h. After that it was dried in an oven at 120 °C for 24 h., and finally calcined in air at 700 °C for 6 h.

C. Characterizations of Catalysts

XRD patterns of all catalysts were measured by using Bruker D8 Advance X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54056$ Å) over an angle 2θ range of 10° - 80° with a resolution of 0.02°.

The specific surface area, average pore volume, and pore size diameter of the catalysts were determined by

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N_2-physisorption using Micromeritics ChemiSorb 2750 Pulse instrument.

Morphology of the catalysts and elemental distribution of a catalyst were investigated by scanning electron microscope (SEM) and energy X-ray spectroscopy (EDX), respectively using Hitashi mode S-3400N

D. Reaction Test

Gas-phase ethanol dehydration was performed to determine the catalytic activity and product selectivity of the alumina-silica composite and H-Beta zeolite catalysts. The reaction system is presented in Fig. 1. The reaction was determined using a fixed-bed continuous flow reactor. For the reaction test, quartz wool and the desired amount of catalyst was packed into the middle of a glass tube reactor. The catalyst was pretreated in nitrogen flow (50 ml/min) at 200 ℃ for 1 h. The ethanol or mixture of ethanol and 1-propanol was vaporized at 120 ℃, and then it was injected into the reactor by a single syringe pump. The dehydration reaction was carried out at 1 atm of total pressure and the temperature ranging between 200-400 ℃. The light hydrocarbon products were analyzed by gas chromatography technique (Shimadzu GC-14B) with flame ionization detector (FID) using capillary column (DB-5).
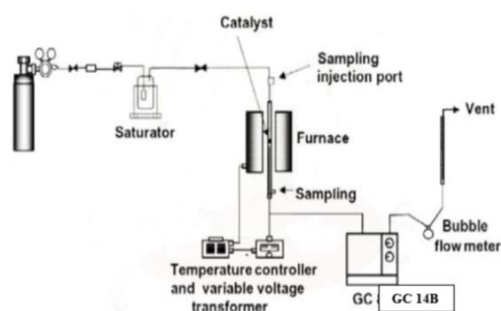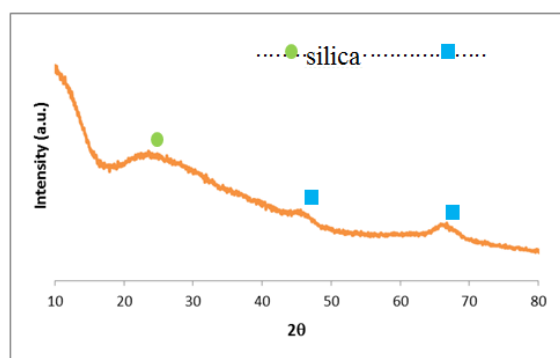

Fig. 1. Flow diagram of dehydration system.

Fig. 2. XRD pattern of the Al_2O_3-SiO_2 catalyst.

III. RESULTS AND DISCUSSION

A. Characteristics of Catalysts

Several techniques were performed to characterize the H-Beta zeolite and Al_2O_3-SiO_2 catalysts. The XRD pattern of the Al_2O_3-SiO_2 catalyst is shown in Fig. 2. The Al_2O_3-SiO_2 catalyst exhibited XRD pattern showing the broad peaks between 21-24° as seen typically for the amorphous structure of silica. Moreover, XRD pattern of this catalyst was appeared the sharp peak around 45° and 67° indicating the presence of γ-Al_2O_3 crystallite [17]. It can confirm that there was alumina and silica in the synthesized Al_2O_3-SiO_2

catalyst.

The textural properties characterized by N_2 physisorption including surface area and average pore size diameter of the catalysts are shown in Table I. It showed that surface area of the H-beta zeolite catalyst was 2 times higher than that of the Al_2O_3-SiO_2 catalyst. On the other hand, the Al_2O_3-SiO_2 catalyst indicated larger average pore size diameter than that of the H-beta zeolite catalyst.

TABLE I: TEXTURAL CHARACTERIZATION OF THE CATALYSTS.

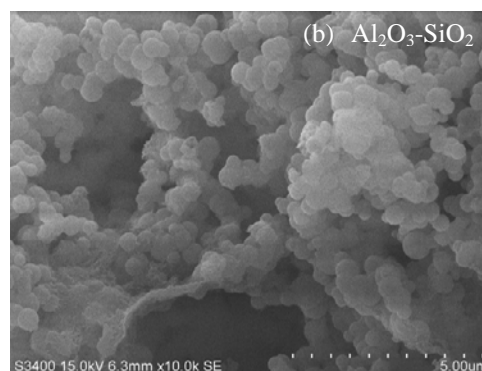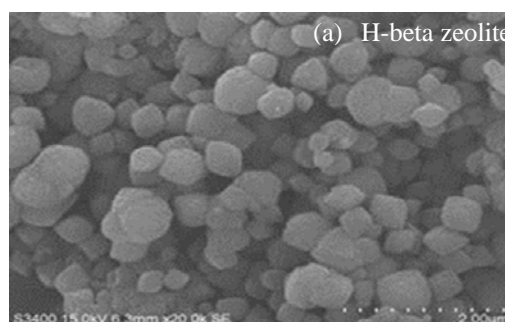| Catalysts	BET surface area (m^2/g)	Average pore diameter (nm)
Al_2O_3-SiO_2	276	5.6
H-Beta zeolite	522	2.2

Fig. 3. SEM photographs of (a) H-beta zeolite and (b) Al_2O_3-SiO_2 catalysts.
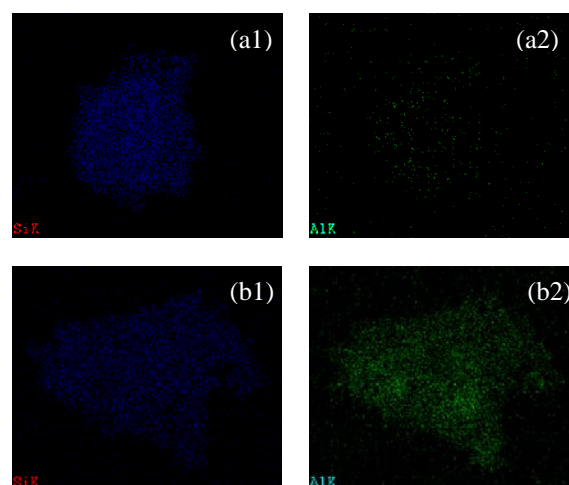

Fig. 4. The typical EDX mapping of (a1) Si (a2) Al distribution on H-beta zeolite catalyst, and (b1) Si (b2) Al distribution on Al_2O_3-SiO_2 catalyst.

The elemental distribution on the catalysts were determined using EDX mapping as shown in Fig. 4. The distribution of Al and Si was measured. For the H-Beta zeolite catalyst, the density of Si was strongly measured but the density of Al was slightly observed. It revealed that Si is a

major component of the H-Beta zeolite catalyst. For the Al_2O_3-SiO_2 catalyst, Al and Si component had the strongly densities on the catalyst surface since both components are the main components of the Al_2O_3-SiO_2 catalyst. Moreover, a good distribution of Al and Si on the surface of the Al_2O_3-SiO_2 catalyst was also observed.
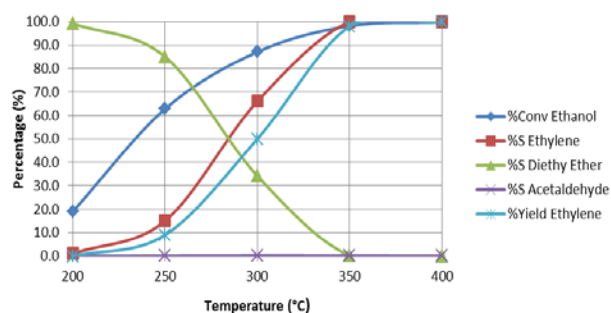

Fig. 5. The results from dehydration of ethanol over H-beta zeolite catalyst.

B. Reaction Test

The catalytic activities of the H-beta zeolite and the Al_2O_3-SiO_2 catalysts were investigated over the dehydration of pure ethanol and mixture of ethanol with propan-1-ol as an impurity. Ethanol dehydration was carried out in temperature ranging between 200 to 400 ℃ and atmospheric pressure. For the H-beta zeolite and the Al_2O_3-SiO_2 catalysts, ethanol conversions increased with increasing the reaction temperature as seen in Fig. 5 and Fig. 6, respectively. Diethyl ether was a main product when the reaction temperature was lower than 250 ℃. Amount of diethyl ether decreased with increasing reaction temperature. On the other hand, ethylene was a major product when the reaction temperature was over 270 ℃ and 290 ℃ for the H-beta zeolite and the Al_2O_3-SiO_2 catalysts, respectively. Thus, selectivity of diethyl ether decreased but selectivity of ethylene increased with increasing the temperature of ethanol dehydration reaction. It can confirm that the reaction temperature is one of significant factors effecting on the ethanol conversion and product selectivity.
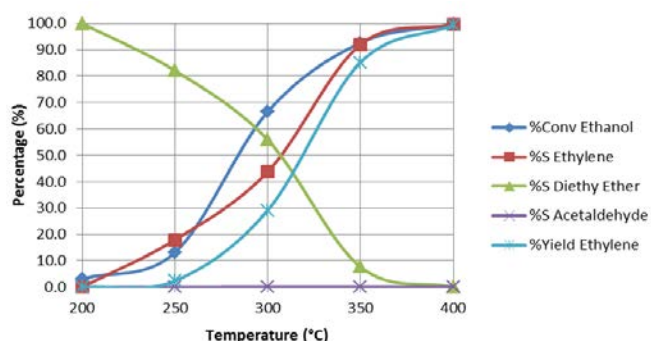

Fig. 6. The results from dehydration of ethanol over Al_2O_3-SiO_2 catalyst.

For comparative performance of the H-beta zeolite and the Al_2O_3-SiO_2 catalysts over the dehydration of pure ethanol, the H-beta zeolite catalyst exhibited higher conversion of ethanol at all reaction temperatures as seen in Fig. 5 and Fig. 6. Ethanol conversion of the H-beta zeolite reached about 100% at lower temperature (~350 ℃) than that of the Al_2O_3-SiO_2 (~400 ℃). This may be because the H-beta zeolite had larger

amount of weak acid site (0.84 mmol NH_3/g catalyst) [18] than the Al_2O_3-SiO_2 (0.57 mmol NH_3/g catalyst) [19]. Normally, weak acid site is identified as a Brønsted acid site which is preferred for ethanol dehydration [20].
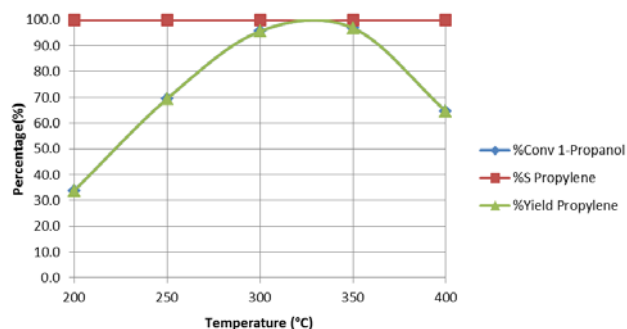

Fig. 7. The results from dehydration of propan-1-ol over H-beta zeolite catalyst.

The dehydration of ethanol mixed with propan-1-ol was performed in order to investigate the effect of propan-1-ol impurity on the catalytic activity and product distribution of the H-beta zeolite and the Al_2O_3-SiO_2 catalysts. Ethanol and propan-1-ol were mixed at a ratio of 96:4 %v/v, and the mixture was used as a reactant for the dehydration reaction instead of a pure ethanol.
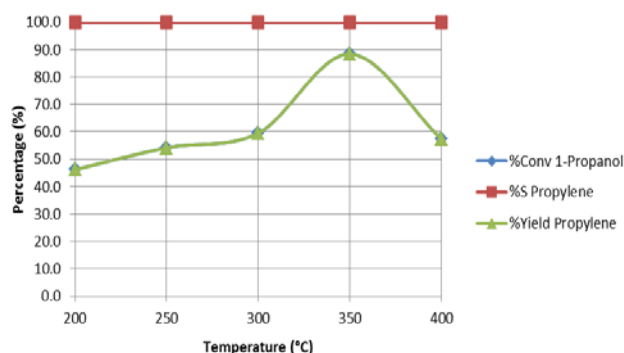

Fig. 8. The results from dehydration of propan-1-ol over Al_2O_3-SiO_2 catalyst.

Conversion and yield of ethanol and propan-1-ol, as well as products selectivity of the H-beta zeolite and the Al_2O_3-SiO_2 catalysts are presented in Fig. 9 and Fig. 10, respectively. The H-beta zeolite catalyst revealed the highest ethanol conversion of 100% at 400 ℃ and the highest ethanol conversion of the Al_2O_3-SiO_2 catalyst was about 49% at the same temperature. This is because the H-beta zeolite catalyst has higher amount of Brønsted acid site, which is preferred for ethanol dehydration, than the Al_2O_3-SiO_2 catalyst [18]-[20]. At 200 ℃, it can be observed that both catalysts presented the highest selectivity of propylene. The Al_2O_3-SiO_2 catalyst exhibited higher propylene selectivity than the H-beta zeolite catalyst between 200 – 300 ℃. Propylene selectivity decreased with raising the reaction temperature conversely the ethylene selectivity. However, for the dehydration of ethanol mixed with propan-1-ol over the H-beta zeolite catalyst, the ethylene selectivity was reduced approximately 2 times compared to the dehydration of pure ethanol. In case of the Al_2O_3-SiO_2 catalyst in the dehydration of ethanol mixed with propan-1-ol, ethylene selectivity was still reached 99% at 400 ℃. This is similar to the result of

pure ethanol. The H-beta zeolite catalyst presented slightly higher ethylene yield (~55%) than the Al_2O_3-SiO_2 catalyst (~48%).
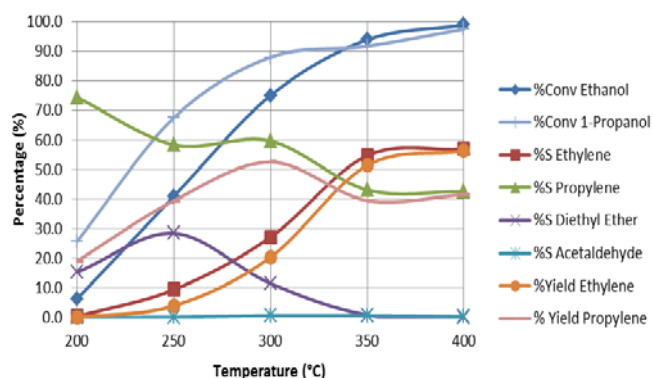

Fig. 9. The results from dehydration of ethanol mixed with propan-1-ol over H-beta zeolite catalyst.

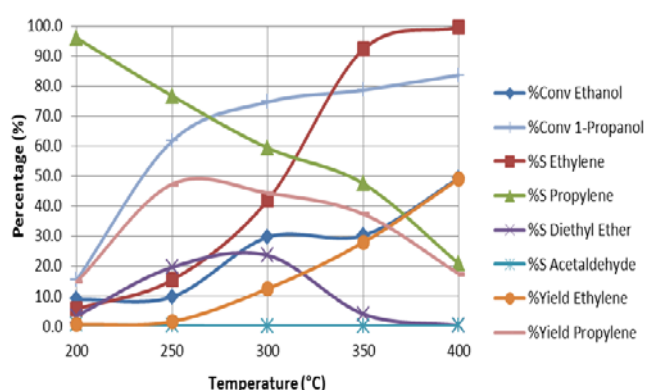Fig. 10. The results from dehydration of ethanol mixed with propan-1-ol over Al_2O_3-SiO_2 catalyst.

IV. Conclusion

The dehydration of ethanol mixed with propan-1-ol as an impurity over the Al_2O_3-SiO_2 catalysts was investigated and compared the results to the H-beta zeolite catalyst. For the Al_2O_3-SiO_2 catalyst, propan-1-ol influenced the ethanol conversion and ethylene yield. They were decreased about 2 times compared to the results of the dehydration of pure ethanol. However, ethylene selectivity of this catalyst for the dehydration of ethanol mixed with propan-1-ol was similar to that of pure ethanol. For H-beta zeolite catalyst, propanol affected the ethanol conversion, ethylene yield, and ethylene selectivity. Ethanol conversion could be achieved 99% but it must be performed at higher temperature than the use of pure ethanol. Ethylene yield and ethylene selectivity were about 45% decreased from the dehydration of pure ethanol. Moreover, propan-1-ol to propylene preferable occurred at low temperature but ethanol to ethylene preferable took place at high temperature.

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