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# Ethanol conversion to selective high-value hydrocarbons over Ni/HZSM-5 zeolite catalyst



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#### ABSTRACT

Bio-ethanol is a renewable fuel and can be converted to high-values chemicals. This study showed that more aromatics and gas products could be obtained at a low weight hourly space velocity (WHSV) than that at high WHSV using HZSM-5 and Ni/HZSM-5 catalysts. A low WHSV offered an increased tendency to build up aromatics and paraffins. Real bio-ethanol broth was tested and gave the similar result as pure ethanol solution. That catalysts could retain full catalytic activity after 168 h in reaction provides evidence for their long stability. This study advantageously demonstrates a promising approach to generate high-value products from bio-ethanol.

## 1. Introduction

Bio-ethanol is one of the most essential and promising renewable energy carriers available today from an environmental and economic point of view [1]. Among methods of converting ethanol, considerable attention has been paid to the catalytic conversion of ethanol to gasoline or highly valuable hydrocarbons.

Depending on the structure of catalysts and the reaction conditions, ethanol can be converted to several high-value products, such as paraffin, olefin, and aromatics. Among candidate catalysts, HZSM-5 zeolite materials have been a topic of discussion. Acid sites promote the dehydration of ethanol to ethylene and other reactions (e.g., oligomerization and cracking) to form higher hydrocarbons, which plays a dominant role in product distribution [2]. With the distinctive design of topological properties, zeolite effectively promotes the selectivity towards the desired hydrocarbons [3]. Several studies focus on metal addition to the HZSM-5 materials; these include Ce [4], Fe [5], Mo [6], La, and Mg [7], Zr [8], and Ni [9,10]. Among candidates, Ni could dramatically produce high carbon oligomers [9,10]. For further finding the optimum conditions, attention has been paid to operational conditions; these include reaction temperature, water content, weight hourly space velocity (WHSV), and time on stream (TOS). Generally, high reaction temperature favors the catalytic activity; however, the

exceedingly high temperature might lead to irreversible deactivation of the HZSM-5 zeolite by dealumination HZSM-5 [11]. The water content in the feed also affects the conversion of ethanol and the distribution of products. The presence of water helps to reduce the amount of coke on the catalyst, resulting in decrease catalyst deactivation. However, high amounts of water might attenuate the rates of desired oligomerization and crack reactions [12]. It is well-known that the dehydration of ethanol to gaseous products, such as ethylene, is a very fast reaction which accepts to be conducted at high WHSV. However, the following reactions to produce the more valuable hydrocarbons, such as paraffin, olefin, and aromatic products, require to be conducted at a low WHSV. For example, WHSV below 4 h<sup>-1</sup> has been shown to increase the selectivity to liquid hydrocarbons. On the other hand, decreasing WHSV far below  $0.5 \text{ h}^{-1}$  does not enhance production of liquid products [13]. In this regard, it is important to note that a significant drop in the selectivity to liquid hydrocarbons has been observed after a sufficiently high time on stream [3,14]. As summarized in Table S-1, the respective reaction conditions, conversion, and product distribution vary considerably in those studies [15-18].

Although HZSM-5 is also a potential candidate catalyst for ethanol conversion [18,19], this process still has some limits and requires extensive studies. For example, there is still a lack of clear and detailed investigations for obtaining a concise insight into the conversion of

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ethanol to gasoline type hydrocarbons using HZSM-5-type zeolites. Importantly, among several concerns that require further insights, selecting suitable reaction conditions for achieving high selectivity to valuable hydrocarbons and stability information of the used catalysts are vital. Therefore, HZSM-5 and Ni/HZSM-5 catalysts are picked up for prolonging the conversion of ethanol into the valuable hydrocarbons in this study.

# 2. Experimental

## 2.1. Preparation of catalysts

The HZSM-5 zeolite was converted from its original ammonium form  $(SiO_2/Al_2O_3 \text{ of } 42.5)$  into its active H-form by calcination at 823 K in the air for 5 h. Following, the calcined zeolite was exchanged by NH<sub>4</sub>NO<sub>3</sub> at 353 K, washed with deionized water, and dried at 393 K in the air for 4 h. The detailed procedure was previously described elsewhere [20]. The 1wt.%Ni/HZSM-5 zeolite was prepared by the incipient wetness method. Typically, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was firstly dissolved in deionized water and then dripped slowly on the HZSM-5 powder. Then, the powder was dried at 353 K in an oven for 8 h, and calcined at 823 K in the air for 5 h.

## 2.2. Characterization of catalysts

The catalysts were characterized by an X-ray diffractometer (XRD, Rigaku) with Cu K $\alpha$  radiation to verify the crystal structure of HZSM-5. Regarding the coke on the spent catalysts, a thermal gravimetric analysis (TGA, Rigaku TG8120) was performed in the temperature range of 383–1073 K. The pore size distribution and BET surface area were determined by N<sub>2</sub> adsorption at 77 K in the relative pressure range of 0.001 to 0.1 using a physisorption Analyzer (Micromeritics ASAP 2020). Fourier transform infrared (FTIR) spectroscopy (Thermo Nicolet, Nexus 470, MCT/A-detector) was conducted to evaluate the Brønsted and Lewis acid sites of zeolites. The acid strength of the catalyst was measured by NaOH titration experiments using indicators [21].

## 2.3. The catalytic activity

An hour of pre-flowing was employed to ensure a steady-state. The ethanol conversion to selective hydrocarbons was carried out in a 1/2in. stainless steel reactor of the reaction system (as seen in Fig. S-1). The weight hourly space velocities (WHSV) and reaction temperatures were controlled in the range 0.5 to  $3.5 \ h^{-1}$  and 473 to 673 K, respectively. Aqueous ethanol solutions (72% and 99.8%, Sigma-Aldrich) was pumped through an evaporator, which was held at 443 K. A Nitrogen (99.99%) stream was used as a carrier gas for the ethanol vapor. To ensure also here a steady-state and that all possible dead volumes are filled, the experiment was first started after 30 min of pre-feeding. All of the stainless steel pipes were heated and insulated at 373 K. A condenser with a temperature of 273 K was connected to the outlet pipe of the reactor to collect liquid products.

During the experiment, a sample was taken every half an hour from the sample loop and analyzed by the online gas chromatographs (GC). The reaction products and reactants were analyzed by three GC: GC-TCD (China Chromatograph, 9800, column: HAYESEP D 80/100, 10 ft.  $\times$  1/8 in.), GC-FID (Hewlett & Packard, HP6890 Series plus, column: Agilent 19,091 N-1113 HP-Innowax, 30 cm  $\times$  320 µm  $\times$  0.25 µm) and GC–MS (Agilent Technologies, 7890, column: HP-5MS, 29.8 cm  $\times$  0.25 mm  $\times$  0.25 µm). GC-TCD analyzed the feeds concentration and gas products; GC-FID analyzed the products in the aqueous phase while GC–MS analyzed the composition of the oil phase.

The conversion rate of ethanol,  $X_{EtOH}$ , was defined as follows



Fig. 1. (a) XRD patterns and (b) FTIR spectra of HZSM-5 and Ni/HZSM-5 catalysts.

$$X_{EtOH}(\%) = \frac{m_{EtOH}^{0} - m_{EtOH}}{m_{EtOH}^{0}} \times 100\%$$
(1)

where  $m_{EtOH}^{0}$  was the overall moles of ethanol, which were fed in the system.  $m_{EtOH}$  was the overall remaining moles of ethanol, which was detected by GC-TCD, GC-FID, and GC–MS.

The selectivity to product i,  $y_i$ , was calculated on a carbon basis by

$$y_{i} = \frac{m_{i} \times n_{i}}{(m_{EtOH}^{0} - m_{EIOH}) \times 2} \times 100\%$$
(2)

where  $m_i$  was the overall moles in one experiment of component *i* and  $n_i$  the number of carbon atoms in component *i*.

# 3. Results and discussion

# 3.1. Characterization of catalysts

As expected, the XRD pattern of the HZSM-5 catalyst exhibits the characteristic signals at  $2\theta = 7.95^{\circ}$ ,  $8.95^{\circ}$ , and  $23.10^{\circ}$  (as shown in Fig. 1(a)). Additionally, it clearly indicates that the Ni metal modified HZSM-5 still retained the HZSM-5 structure with only slightly less ordered structures. It can also be noted that the Ni metal was well-dispersed as a form of nanoparticle on the surface of the HZSM-5, resulting in no significant XRD signals detected. Table S-2 shows the specific surface area and average pore size of HZSM-5 and Ni/HZSM-5 catalysts

indicating both catalysts have high surface areas (334.0 and 413.2  $\text{m}^2.\text{g}^{-1}$ , respectively). Note that the presence of Ni-modified might locate on the external surface and block the HZSM-5 micropores, leading to reduce the BET surface area. Concerning the average pore size, Ni/HZSM-5 catalyst has a similar average pore size, which is slightly larger than that for HZSM-5.

The acid strength, i.e., pKa values, for both HZSM-5 and Ni/HZSM-5 were in the range of -5.6 to -8.2 listed in Table S-3. To further investigate the acid sites on the catalysts, the ratio of Lewis to Brønsted (L/B ratio) acid sites was determined by FTIR spectroscopy, as shown in Fig. 1(b). The wavenumbers at 1550, 1450, and 1490  $\text{cm}^{-1}$  are attributed to Brønsted. Lewis acid sites, and a combination of Lewis-Brønsted acidity [22]. It shows clearly that the presence of Ni-metal influences the acidity property, their combined Lewis-Brønsted acidity, and Brønsted acid sites were lower than that of unmodified HZSM-5 zeolite. On the contrary, the intensity of the assigned peak for the Lewis acid site of Ni/HZSM-5 was higher than that of unmodified HZSM-5 zeolite. The results of comparing the areas under the peaks are listed in Table S-2. Clearly, the L/B ratio of unmodified HZSM-5 catalyst was lower than that of Ni/HZSM-5, which indicates it had the most Brønsted acid sites. In previous studies, of the presence of metal, such as Fe [23], Ni, Ga, Fe [10], are also found to influence the acidity property of parent HZSM-5 zeolite.

## 3.2. Ethanol conversion

As shown in Fig. 2, HZSM-5 performed a good ethanol conversion to selective olefins, paraffins, and aromatics, which own valuable fuel properties [10]. Modified Ni/HZSM-5 would alter the acidity property of parent HZSM-5, thus increase the ratio of Lewis to Brønsted (L/B ratio) acid sites, leading to enhance the catalytic conversion ethanol from 84 to 88% to 90–92% under same reaction conditions. However, the maximum difference with 5% is not significant. On the other hand, it notes that the introduction of Ni, which might alter the catalytic mechanism, is not used for increasing the yields of aromatics and the combined liquid paraffins and olefins.

The effect of experimental conditions, such as reaction temperature, total time on stream (TOS), WHSV, feed concentration of aqueous ethanol solution, the percentage of coke mass retained on spent catalysts (by TGA) is summarized in Table S-4. The proportion of coke mass retained on spent catalysts is dependent on the reaction temperature and TOS. By contrast, it is found that the coke has no significant changes with different WHSV (0.5, 1.8, and 3.5 h<sup>-1</sup>). Galadima and Muraza pointed out that the narrow channel systems of HZSM-5 zeolites inhibit the coke deposits [3]. This result is consistent with our finding that the effect of WHSV on coke accumulation is not remarkable in this study. On the other hand, the influence of feed concentration of aqueous ethanol solution on the percentage of coke mass retained was insignificant.

Fig. 2(a) shows the influence of reaction temperature in the conversion of ethanol and the corresponding product distributions. The study focuses on the range of temperature of 573–673 K. The maximum temperature studied, 673 K, is set to avoid irreversible deactivation by the dealumination of the HZSM-5 zeolite [11]. There is only a slight impact on the conversion of ethanol and the selectivity of particular products. The aromatic fraction is of particular interest. The increase in temperature affects the reaction pathway to form more aromatics, which are favorable in comparison to paraffin and olefin products. According to Schulz et al., gaseous products, such as ethylene or diethyl ether, might repeatedly be inserted into ethanol molecule that is chemisorbed on the catalyst surface at high reaction temperatures [24]. As a result, more long aliphatic chains can be formed that might be readily converted to aromatic and paraffin products under the conditions used. The observed effects support the assumption that gaseous products, such as ethylene and/or diethyl ether, are the primary products of ethanol conversion at the low reaction temperature. When the temperature is further increased, subsequent reactions are anticipated to lead to the formation of liquid products, such as aromatic, olefin, and paraffin products. In line with this, Wu et al. proposed that ethanol conversion is promoted with increased reaction temperature over  $TiO_2/$  zeolite catalysts [25]. At high reaction temperature, such as in the range of 573–723 K, the activity would be shifted towards the formation of paraffin, aromatic products. These results are consistent with our observation.

Fig. 2(b) shows the effect of WHSV on the conversion of ethanol and product distributions under a reaction temperature of 623 K using an ethanol feed concentration of 99.8 wt% over HZSM-5 and Ni/HZSM-5 catalysts. Overall, the conversion of ethanol over the Ni/HZSM-5 catalvst is above 90% for all WHSV conditions. This value remains almost constant and is slightly higher than that over the HZSM-5 catalyst, which is in the range of 84-88%. It notes that the WHSV has a strong influence on the distribution of products. At high WHSV, gaseous products such as ethylene, are the primary products which are formed by the dehydration reaction of ethanol using HZSM-5. However, Ni/HZSM-5 shows no significant difference in the selectivity of gaseous products, but liquid products. More aromatic products tend to be produced when the WHSV is decreased for both catalysts. The prolonged reaction time promotes the formation of longer aliphatic chains resulting in the creation of paraffin, olefin, and aromatic products on HZSM-5 [24,26]. By contrast, Ni/HZSM-5 could obtain more valuable aromatic and gas products at low WHSV, indicating a potential to make separation easily.

The effect of water content in ethanol (0.2-28.0 wt%) was fully studied under designed conditions (reaction temperature of 623 K, WHSV of 1.8  $h^{-1}$ ). According to Schulz et al., water was eliminated during the dehydration reaction of ethanol over zeolites; therefore, water should have no particular effect on the selectivity to products [24]. As expected, Fig. 2(c) shows that not only the product distribution but also the conversion of ethanol is similar for both concentration values (28.0 wt% and 0.2 wt% of water content, respectively) in the cases of the HZSM-5 and Ni/HZSM-5 catalysts. Similarly, the previous study shows that the conversion of ethanol/water mixtures and the selectivity to products over the HZSM-5 catalyst were relatively insensitive to a given range of water content [24]. On the other hand, Oudejans et al. reported that formation of aromatics over HZSM-5 catalyst increased with an increasing amount of water (up to a molar ratio water/ethanol = 1), then became constant at molar ratios water/ ethanol > 1 at a WHSV of 0.07 h<sup>-1</sup> and reaction temperature of 578 K [27]. In our study, a real bio-ethanol broth by fermentation was also tested. A vapor stream near 72 wt% ethanol, which was distilled from real bio-ethanol broth, was used to carry out the reaction at the same conditions. We found that some impurities of real bio-ethanol (Table S-5) have a negligible influence on the ethanol conversion. Fig. S-2 shows that a similar performance could be achieved for both the real bioethanol and pure ethanol contained 28.0 wt% of water content. A lifetime study has been conducted with a total time on a stream of 168 h in order to investigate the stability behavior of the catalysts. Fig. 3 shows that both HZSM-5 and Ni/HZSM-5 exhibit a stable conversion value of 87-92% during 168 h in reaction. Although the coke on catalysts surfaces increased during the reaction (Table S-4), there is an insignificant change in the catalytic activity. Importantly, catalysts could repeatedly be conducted without any loss in catalytic performance. For the production distributions, Fig. 3 also reveals that the yields of aromatic products have a tendency to decrease while that of gaseous products to increase, and liquid products stay relatively constant during the reaction. The possible reason is that ethanol is firstly converted into gaseous products through dehydration reactions. Then, secondary reactions which might be catalyzed by different active sites lead to the formation of liquid products, such as aromatic, olefin, and paraffin products. This result is in agreement with a previous study [24].



**Fig. 2.** Product distribution and ethanol conversion for HZSM-5, Ni/HZSM-5 catalysts: (a) Different reaction temperatures under WHSV of  $1.8 h^{-1}$ , ethanol feed conc. of 99.8 wt%; (b) Different WHSV under a reaction temperature of 623 K, ethanol feed conc. of 99.8 wt%; (c) Different water content under reaction temperature of 623 K, WHSV of  $1.8 h^{-1}$ .

# 4. Conclusions

Conversion of ethanol to selective hydrocarbons was successfully investigated by using HZSM-5 based catalysts. Both of HZSM-5 and Ni/ HZSM-5 catalysts showed good ethanol conversions. Under the same reaction temperature, the reaction over Ni/HZSM-5 catalyst, which was conducted at low WHSV, led to a higher selectivity towards valuable aromatic than that at high WHSV. A similar product distribution was found for HZSM-5 and Ni/HZSM-5 catalysts under different ethanol feed concentration and the real bio-ethanol. A low WHSV promoted the formation aromatic products. Both H-ZSM-5 and Ni/H-ZSM-5 exhibited stable conversions of 87% and 90%, respectively, in long 168-h



Fig. 3. The time on stream of ethanol conversion and their corresponded selectivity to products over (a) HZSM-5, and (b) Ni/HZSM-5 catalysts. Experimental conditions: ethanol concentration of 72%; operating temperature of 623 K; WHSV of 1.8  $h^{-1}$ .

reaction.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

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