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Ethylene production via ethanol dehydration over desilicated ZSM-5 catalyst

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ABSTRACT

The catalytic dehydration of ethanol is a potential alternative route to synthesize ethylene apart from the traditional method which depends on fossil fuels. This report successfully prepared modified ZSM-5 with mesopores using desilication methods to enhance ethanol catalytic dehydration performance and ethylene production at lower temperature. The modified zeolite have the external surface area increased by 3.5 times and a higher dehydration efficiency compared with the original sample especially at temperatures below 220°C. Increasing reaction temperatures and gas houly space velocity (GHSV) increased the dehydration efficiency while increasing the inlet ethanol concentration had opposite effect. Significantly, the ethanol conversion over modified zeolite remained above 90 % when the GHSV increased to 36000 h^{-1} after the time-on-stream of 24 h.

Introduction

Ethylene is one of the most demanding organic compounds in the chemical industry as it is the key component in the production of common polymers (e.g. polyethylene), surfactants (e.g. ethylene glycol, ethylene oxide). The traditional route of producing ethylene is steam cracking hydrocarbons and it remains the most dominant method [1].

However, to reduce gas emissions and dependency on restricted fossil fuels, the green alternatives for producing ethylene have received more attention in recent years and leading this green trend is the catalytic ethanol dehydration process.

In an attempt to make this process more industrial friendly, several studies have investigated different catalysts to extend ethylene yield and lower reaction temperature. Potential catalysts includes alumina and transition metal oxides, silicoaluminophosphates (SAPO), heteropolyacid catalysts, etc [2].

Due to its unique shape selectivity, solid acid catalytic sites, pore size, ion exchangeability, thermal stability [3] and its possibility of catalyzing the reaction at lower temperatures, microporous ZSM-5 zeolite is a promising material for the catalytic dehydration of ethanol [4]. The acidity of ZSM-5 has a significant impact on the performance of the reaction. However, acid sites concentrate deep within the microporous network which makes it difficult for the reactant molecules to reach due to the resistance of diffusion [5]. Zeolites composed of micro- and mesopores can overcome this limitation and this material can be synthesis using a wide range of methods such as zeolitization, double templating, recrystallization, dealumination and desilication, etc [6].

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In this paper, a commercial ZSM-5 has been simply modified to increase the mesoporosity by a desilication method. The catalytic activity of ethanol dehydration to produce ethylene at various reaction conditions are reported. The enhancement of ethanol conversion as well as ethylene selectivity have been observed over the mesoporous ZSM-5 catalyst.

Experimental

Catalyst preparation

Mesoporous zeolite was prepared using desilication method reported in previous study [7] with modification. Firstly, 100 ml of 0.2 M NaOH solution was heated to 65 °C. Then, 3.3 g of zeolite ZSM-5 (Si/Al=200, provided by Wasol Co.) was added to the solution and was stirred vigorously. After 30 min, the slurry was cooled down immediately using an ice bath. It was filtered and carefully washed until neutral pH and dried at 80 °C overnight. The zeolites were converted to acid form via ion exchange technique using NH_4Cl 1M. The process was repeated three times with fresh NH_4Cl solutions followed by calcination at 350 °C for 3 h. The original ZSM-5 and the modified ZSM-5 were labelled M0 and M1, respectively.

Catalyst characterization

The crystalline structure of the prepared zeolites was analyzed by X-ray diffraction (XRD, diffraction D8), operating with Cu Kα radiation (=1.5418 Å) at 40 kV and 30 mA. The XRD pattern was collected in the range 2θ of 5° - 50° with a 0.019 step size. The samples were also characterized by scanning electron microscope (SEM) using Hitachi FE SEM S-4800, the BET surface area and mesoporous area of the materials were determined using the NOVA 2200e Surface area and Pore size analyzer (Quantachrome Corp.). The Brønsted acidity of zeolite was determined using the conductometric titration method [8].

Ethanol dehydration experiments

The ethanol catalytic dehydration experiments were performed under a controlled condition with temperature ranging from 140 to 340 °C, gas hourly space velocity (GHSV) ranging ranging from 6000 to 36000 h^{-1} and ethanol concentration of 1.5, 4.2 and 10.3 % v/v. The zeolite samples were pressed, crushed, and sieved. Then, 0.2 g of zeolite was fixed in the reaction tube between 2 layers of glass wool. The ethanol in the stream was generated by bubbling method. The ethanol was fed to reactor by pure nitrogen (> 99.99 %) under defined temperature conditions. Flow rate is adjusted by needle valve and controlled by flow meter. A three-way valve, which was connected with the outlet of the chamber, separated the flow into two streams, a bypass stream and a stream to the reactor.

The reaction process consisted of 3 phases: (1) Catalyst activation was performed in situ in nitrogen for 2 h at 400 °C. (2) Ethanol was fed into the system by switching the 4-way valve to allow nitrogen flow to pass through the ethanol container. The two 3-way valves were switched to bypass state to first stabilize the ethanol concentration. (3) The 3-way valves were adjusted so that the feed flow passed through the reactor. The outlet was transferred to a toluene container to absorb the unreacted ethanol. The final flow contained ethylene and toluene vapor entered the gas chromatography. The gas stream was analyzed on-line by a Flame Ionization Detector (FID) in gas chromatography (Hewlett Packard 5890plus) which equipped with a six-way valve for online injection.

The conversion efficiency of ethanol was calculated using the following equation:

$$\chi = \left(1 - \frac{C_{out}}{C_{in}}\right) \times 100$$

where χ is the conversion efficiency, $C_{out/in}$ is the outlet/inlet concentration of ethanol.

The concentration of ethylene was determined using toluene as the internal standard and thus was calculated using the following equation:

$$C_{ethylene} = \frac{7}{2} \times \frac{S_{ethylene}}{S_{toluene}} \times C_{toluene}$$

where *C* is the vapor concentration (ppm_v) and *S* is the area of the chromatographic peak.

Results and discussion

The conductometric titration curves of zeolite samples are illustrated in Figure 1 and the calculation of Brønsted acid sites is summarized in Table 1. From the curves of M0 and M1, it is observed that the amounts of OH^- added were 0.058 and 0.066 mmol, respectively. The calculated Bronsted acidity of M1 in Table 1 is slightly higher than M0 as the desilication process decreased the SiO_2/Al_2O_3 ratio in HZSM-5

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zeolites leading to an increase in the number of Bronsted acid sites in material.

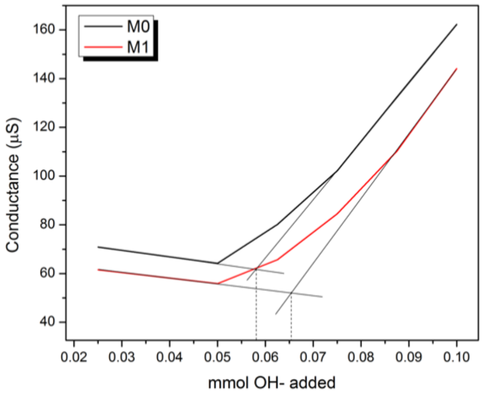

Figure 1: Conductometric titration curve for M0 and M1 titrated with 0.05 M NaOH

Table 1: Bronsted acidity as determined by conductometric titration

Sample	OH$^-$ added (mmol)	[H$^+$] (mmol/g)
M0	0.058	0.29
M1	0.066	0.33

The XRD patterns of both samples are shown in Figure 1. All samples' XRD patterns were consistent with typical X-ray patterns of MFI-type zeolite structure (JCPDS 49-0657), for which the main characteristic peaks appeared at 2θ of 7.8, 8.7, 23.1, 23.8 and 24.3, corresponding to (101), (111), (501), (303) and (313), respectively [9]. The average crystallite size calculated with the Debye-Scherrer equation are summarized in Table 2.

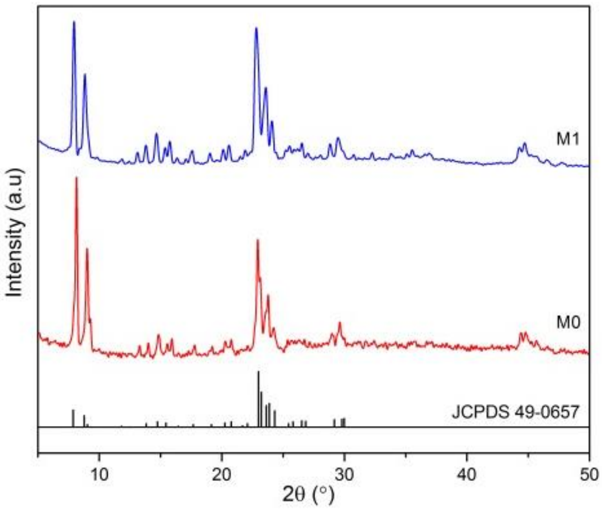

Figure 2: XRD patterns of the catalyst M0 (parent ZSM-5) and M1 (modified ZSM-5)

Zeolite particles were not uniform in size after the preparation process, as shown in Figure 3. The preparation method of mesoporous zeolite material is top-down, where the desilication of zeolite occur randomly in the zeolite structure. Therefore, the modified process can create particles with a wide range of size.

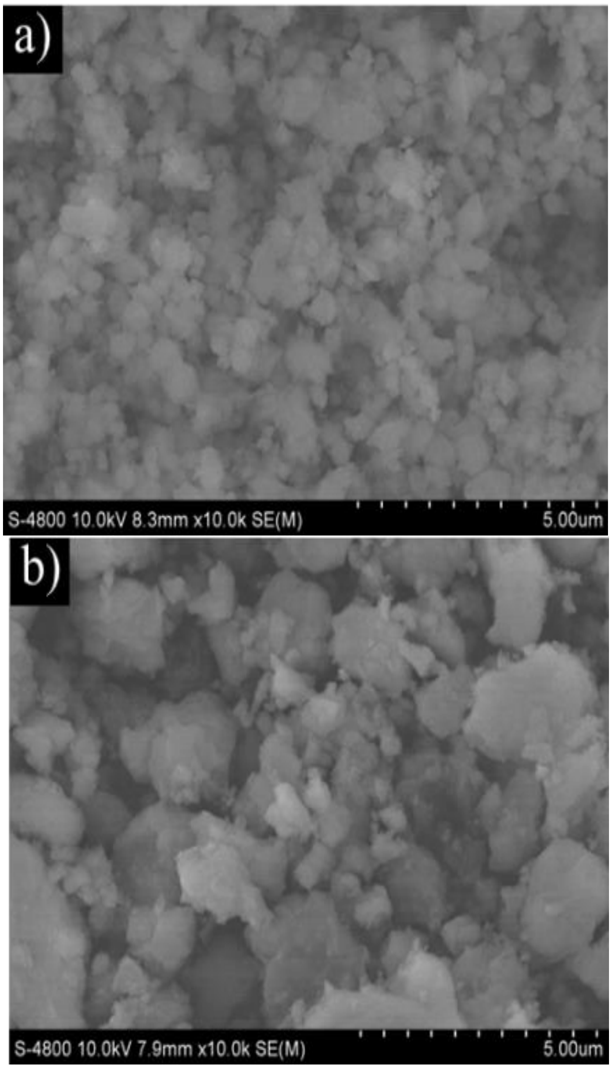

Figure 3: SEM images of (a) M0 (parent ZSM-5) and (b) M1 (modified ZSM-5)

The textural properties of the samples were investigated with N_2 physisorption measurements as shown in Table 2. The specific surface area of modified samples exhibited minor change compared to that of the initial sample (M0) which indicated that the porous structure didn't collapse after the preparation. The surface area of the micropore and mesopore calculated by the t-plot method showed that the external surface area of M1 was 3.5 times higher than that of M0.

Table 2: Surface and structural characterization of the samples

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)[a]	S_{meso} (m^2/g)[a]	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	Crystallite size (nm)[b]
M0	275.8	259.1	16.7	0.20	0.11	24.7
M1	288.7	230.0	58.7	0.23	0.09	30.9

[a] Measured by t-plot method. [b] Measured by the Debye-Scherrer equation

Figure 4 illustrated the effect of reaction conditions (temperature, GHSV, ethanol concentration) on the performance of dehydration of ethanol to ethylene.

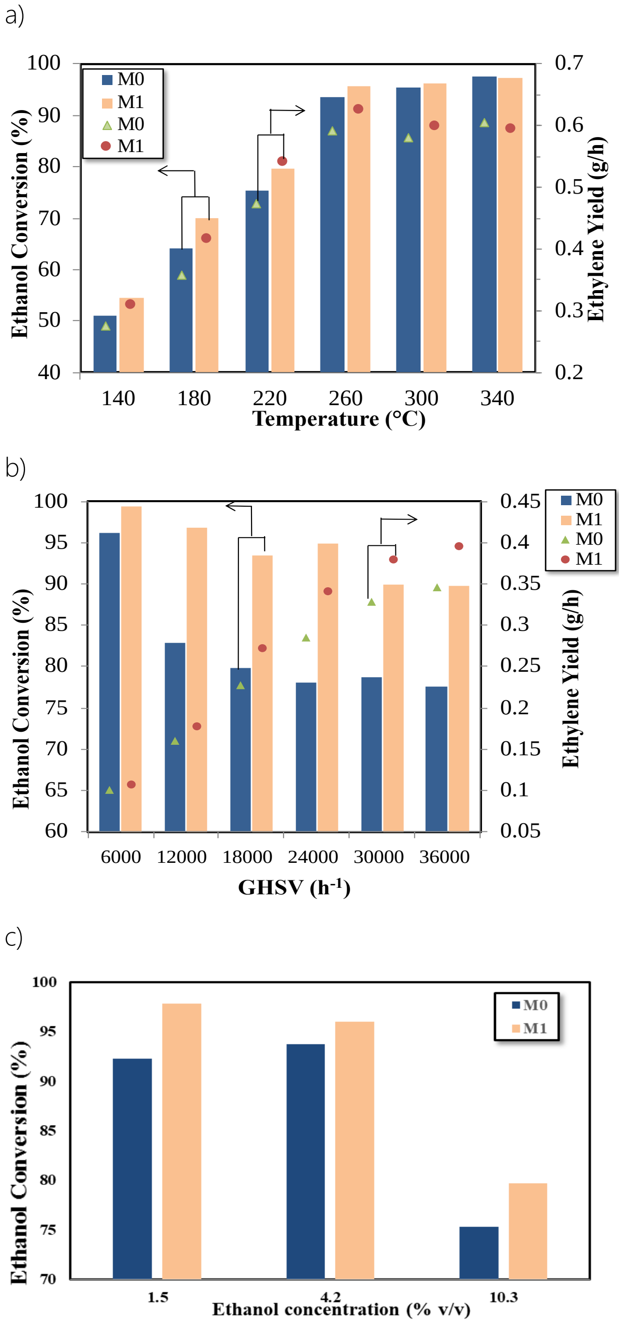

Figure 4: The effects of reaction condition on the dehydration reaction: (a) temperature, (b) GHSV and (c) ethanol concentration

From Figure 4a, the conversion of ethanol of both samples was about 95 % at the reaction temperature from 260 °C. At the lower reaction temperature (140-220 °C), the reaction efficiency decreased but M1 still exhibited higher performance than M0 with the ethanol conversion and ethylene yield of 54.5-79.7 % and 0.31-0.54 g/h, respectively. At 260 °C, M1 displayed higher ethanol conversion with industrially used commercial γ-Al_2O_3 (ethanol conversion = 85 % at 250 °C) [10] and mesoporous silica (ethanol conversion = 35 % at 250 °C) [11]. On the other hand, the conversion of ethanol decreased as the GHSV increased from 6000 – 36000 h^{-1}(Figure 4b). However, the impact on the efficiency of M0 and M1 was different. Specifically, when the GHSV increased from 6000 to 12000 h^{-1}, the ethanol conversion over M0 dropped by approximately 14 % while that of M1 was only about 3 %. These differences were clearly observed in high GHSV because the diffusion of ethanol into the pores was more efficient with the mesoporous material. Figure 4c showed the effect of ethanol concentration to the dehydration efficiency. When the ethanol concentration increased from 1.5 to 4.2 % v/v, the change was insignificant. However, as the concentration reached 10.3 % v/v, the M0 and M1 exhibited a 20 % and 15 % drop in catalytic performance, respectively. As the reactant concentration increases, there will not be enough active sites for catalyzing the dehydration reaction. This will lead to the decrease in ethanol conversion efficiency.

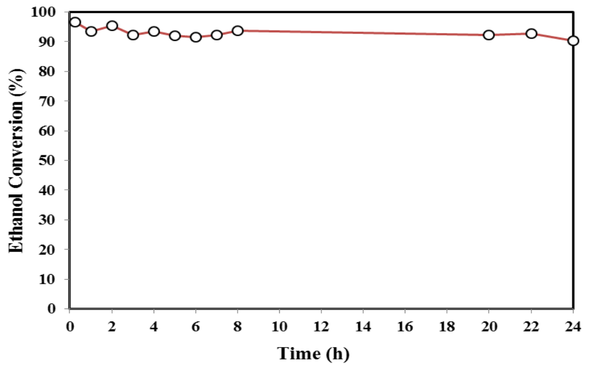

Figure 5: Stability of M1 during ethanol dehydration reaction

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The experiment of catalyst stability was carried out with a concentration of ethanol of 10.3 % (v/v), GHSV of 18000 h^{-1} and a reaction temperature of 220 °C. The conversion of ethanol of M1 after 24 h did not change significantly, as shown in Figure 4. This result suggested that the modified zeolite might improve the catalyst's ethylene yield without sacrificing its stability.

Conclusions

The mesoporous zeolite ZSM-5 was successfully prepared from a commercial zeolite by a simple top-down approach and its characteristics was investigated through XRD, BET, and SEM. The external surface area was increased 3.5 times after the modification process while the material preserved microporous structure for MFI type zeolite. The catalytic activity of ethanol dehydration of the parent ZSM-5 and mesoporous ZSM-5 was investigated based on the change of factors: the reaction temperature, the initial concentration of ethanol, and the flow rate. The mesoporous ZSM-5 had shown higher efficiency than the parent ZSM-5 in dehydration reaction, especially at high GHSV. The overall ethanol catalytic dehydration performance of modified zeolite sample in this study is highest at temperature above 260°C, GHSV of 36000 h^{-1} and ethanol concentration of 10.3 % v/v. The maximum ethanol conversion and the ethylene yield were approximately 97 % and 3 $g/g_{catalyst}/h$, respectively.

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