CHAPTER V
CATALYTIC STABILITY OF THE HIERARCHICAL MESOPOROUS $MSU\text{-}S_{ZSM\text{-}5}$ IN BIO-ETHANOL DEHYDRATION

5.1 Abstract

For the transformation of bio-ethanol into hydrocarbons using a heterogeneous catalyst, time-on-stream is the one of parameters that affects the potential of the catalyst. In this work, the catalytic stability of a hierarchical mesoporous $MSU\text{-}S_{ZSM\text{-}5}$ had been studied for the catalytic dehydration of bio-ethanol. The $MSU\text{-}S_{ZSM\text{-}5}$ was synthesized by using TPAOH as a structure directing agent, and CTAB as a surfactant. The reaction was conducted in a U-tube fixed bed reactor at 450 °C for 4 days to study the reactivity and hydrothermal stability of the catalyst during the catalytic dehydration of bio-ethanol. The characterization of the catalysts was performed by XRD, XRF, TG-DTA, and SAA. The results showed that the synthesized $MSU\text{-}S_{ZSM\text{-}5}$ had pore size around 2.7 nm. The results exhibited that the catalyst still had the potential to transform bio-ethanol into hydrocarbons through 96 hours time-on-stream. Ethanol conversion was 99 %, and ethylene was the main product in the gas stream. For the oil composition, C_{10+} aromatics was the main fraction in oil, followed by C_9 aromatics, benzene, and xylenes, accordingly. Furthermore, C_9 aromatics, benzene, and xylenes selectivities tended to increased adversely with C_{10+} aromatics selectivity, which tended to decrease with time-on-stream.

5.2 Introduction

The social awareness on development of sustainable energy has been increasing worldwide. Many researchers have been trying to find alternative sources of energy. One of the best alternative sources is biomass because it is renewable resource. Bio-ethanol can be produced by fermentation of agricultural feedstocks, and with a 99.5 % purity, it can be blended with gasoline or diesel to be gasohol or bio-diesel. Moreover, bio-ethanol can be used as a feedstock in the catalytic dehydration of bio-ethanol to hydrocarbons.

Many catalysts have been studied in the catalytic dehydration of bio-ethanol. Previous research studies investigated the productions of light olefins such as ethylene (Zhang *et al.*, 2008; Chen *et al.*, 2010), propylene (Meng *et al.*, 2012; Furumoto *et al.*, 2011), and aromatics (Machado *et al.*, 2005). Subsequently, especially for HZSM-5 catalyst, it exhibited a high potential to transform ethanol to hydrocarbons. HZSM-5 can produce valuable hydrocarbons such as benzene, toluene, and xylenes (Inaba *et al.*, 2006). Ethanol to gasoline (ETG) process was studied by Viswanadham *et al.* (2012) by varying acidity and porosity. The results showed that the nano-crystalline ZSM-5 gave higher gasoline yield than micro crystalline HZSM-5 due to its higher acidity and stacking order of mesoporosity.

Although zeolites have a potential to transform ethanol into hydrocarbons, because of their microporous system, they have diffusion limitation for large hydrocarbon molecules. So, mesoporous catalysts such as MCM-41 on ethanol dehydration had been studied. However, because of its poor framework stability and poor acidity, the mesoporous catalyst was not capable to use as the catalysts on ethanol dehydration. To enhance the stability and acidity of MCM-41, several strategies have been investigated such as pH adjustment (Lindlar *et al.*, 2000), addition of acid to the gel during synthesis (Luechinger *et al.*, 2003), change of surfactant type (Lin *et al.*, 1997), and even utilization of micro-mesoporous composite catalyst (Liu *et al.*, 2000, 2001). Subsequently, in 2001, Liu *et al.* synthesized the hierarchical mesoporous MSU-S with ZSM-5 (MSU-S_{MFI}) and Beta (MSU-S_{BEA}) seeds. The results showed that MSU-S_{MFI} and MSU-S_{BEA} provided the higher hydrothermal stability and catalytic activity than Al-MCM-41. Moreover, MSU-S had been used in other reactions. Triantafyllidis *et al.* (2007) studied MSU-S_{BEA} for biomass pyrolysis, and stated that the MSU-S_{BEA} selectively produced polycyclic aromatic hydrocarbons, and provided higher aromatic yields than Al-MCM-41 due to its stronger acid sites.

For the catalytic dehydration of bio-ethanol, the hierarchical mesoporous MSU-S_{BEA} also has been studied by Sujeerakulkai and Jitkarnka (2014). The synthesized MSU-S_{BEA} with Si/Al_2 ratio of 81 possessed the large pore size of about

2.72 nm and high surface area of around 580 m^2/g. The results from bio-ethanol dehydration exhibited that ethylene was the major component in the gas stream whereas C_{10}- aromatics was the main component in the oil composition. followed by C_9 aromatic and xylenes. Moreover. methanol dehydration by using the hierarchical mesoporous MSU-S_{ZSM-5} was studied by Rashidi *et al.* (2013) aiming to produce dimethyl ether (DME). The synthesized MSU-S_{ZSM-5} with SiO_2/Al_2O_3 ratio of 55 gave 100 % DME selectivity in that temperature range of 200 – 320 °C. which was higher than that obtained from Al-MCM-41

From the literatures review. it is evident that the hierarchical mesoporous MSU-S_{ZSM-5} had higher catalytic activity and hydrothermal stability on methanol dehydration to DME than Al-MCM-41. So, in this work. the hierarchical mesoporous MSU-S_{ZSM-5} was studied in the catalytic dehydration of bio-ethanol in order to investigate the product distribution and catalytic stability with time-on-stream (TOS). The reaction was performed at 450 °C under atmospheric pressure for 4 days.

5.3 Experimental

5.3.1 Catalyst Preparation

5.3.1.1 Synthesis of MSU-S_{ZSM-5}

10.2 g of tetrapropyl ammonium hydroxide (TPAOH, 40 %wt) was mixed with 79.26 g of deionized water. Then, 6.0 g of fumed silica and 0.34 g of sodium aluminate as a silicon and aluminum source were sequentially added into the solution of TPAOH and deionized water. The solution was then stirred at 50 °C for 18 hours to form the ZSM-5-seed containing solution. After that. 9.44 g of CTAB were mixed with 100 g of deionized water, and mixed with the solution of ZSM-5-seed. The final gel was kept in a Teflon-lined autoclave for the hydrothermal treatment at 150 °C for 2 days to form the mesoporestructure. Then, the final gel was filtered, washed, and dried. The obtained white powder was ion exchanged with 0.1M NH_4NO_3 in 96 % ethanol at 80 °C reflux temperature for 2 hours. The final catalyst was dried, and calcined at 1 °C/min to 550 °C kept for 10 hours (Liu *et al.*, 2001; Rashidi *et al.*, 2013). Then, the calcined MSU-S_{ZSM-5} was pelletized. crushed.

and sieved into 20 - 40 mesh particles before use in the reactor. The abbreviations of catalysts used in the experiment are shown in Table 5.1.

5.3.2 Catalyst Characterization

Both of small- and wide-angled XRD spectra of the zeolites were determined by Rigaku SmartLab®. For the small-angle mode, the machine collected the data from 1° – 7° at 1°/min. For the wide-angle mode, the machine collected the data from 5° – 50° at 5°/min. The Si/Al ratio of the synthesized MSU-S_{ZSM-5} was determined by XRF. The surface area (BET), pore volume (Horvath Kawazoe method), and pore size (Barrett-Joyner-Halenda method) were determined based on N_2 physisorption using the Thermo Finnigan/Sorptomatic 1990.

Table 5.1 Nomenclature of catalysts used in the experiments

# of run	Catalyst	Abbreviation
1	MSU-S_{ZSM-5} with time-on-stream 1 day	MSU-Z-S1
2	MSU-S_{ZSM-5} with time-on-stream 2 days	MSU-Z-S2
3	MSU-S_{ZSM-5} with time-on-stream 3 days	MSU-Z-S3
4	MSU-S_{ZSM-5} with time-on-stream 4 days	MSU-Z-S4

5.3.3 Bio-ethanol Dehydration

99.5 % purity bio-ethanol was obtained from Sapthip Co.Ltd.,. The catalytic dehydration of bio-ethanol was performed in a U-tube fixed bed reactor under atmospheric pressure at 450 °C for 24, 48, 72, and 96 hours using 3 g of catalyst. Bio-ethanol was fed at 2 ml/hour and mixed with helium co-fed at 13.725 ml/min. The ethanol concentration was determined by a GC-FID (Agilent 6890N), and gas compositions were analyzed by a GC-TCD (Agilent 6890N). The liquid product was condensed in the collector in an ice bath. Then, CS_2 was used to extract the oil from the liquid products. After that, SIMDIST GC was used to determine the true boiling point curve of oil. The range of boiling point indicates the type of petroleum products; <149 °C for gasoline, 149-232 °C for kerosene, 232-343 °C for gas oil, 343-371 °C for light vacuum gas oil, and >371 °C for high vacuum gas oil

(Dũng *et al.*, 2009). The oil composition was determined by using Gas Chromatograph equipped with a Mass Spectrometry of "Time of Flight" type (GC×GC- TOF/MS) (installed with Rxi-5SilMS and RXi-17 consecutive columns). The conditions were set as follows: the initial temperature of 50 °C held for 30 minutes, the heating rate of 2 °C/min from 50 to 120 °C, and 10 °C/min from 120 to 310 °C with split ratio of 5.

5.4 Results and Discussion

5.4.1 Characterization of the Synthesized MSU-S$_{ZSM-5}$

The crystallographic spectra of the hierarchical mesoporous MSU-S$_{ZSM-5}$ determined by using Rigaku Smartlab® in the small-angle mode (SAX) (1-7°) and wide-angle (5-50°) mode are shown in Figures 5.1 (a) and (b), respectively, which indicate that MSU-S$_{ZSM-5}$ semi-crystalline structure was successfully synthesized.

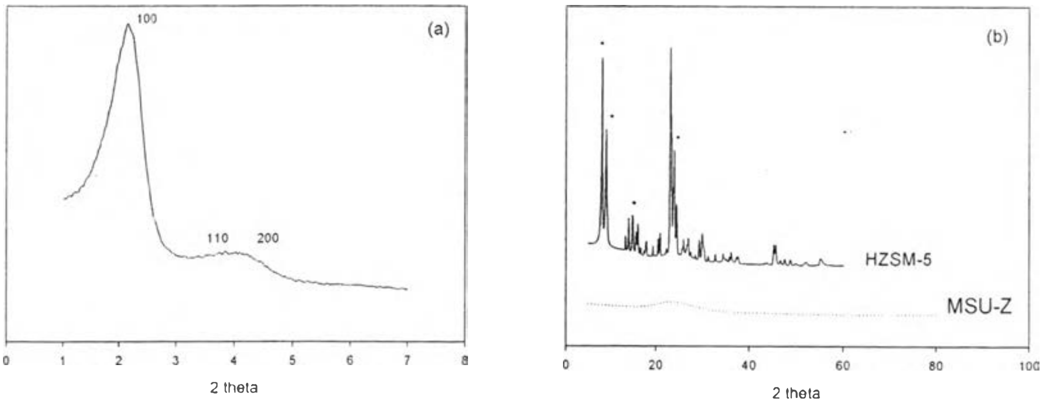

Figure 5.1 (a) SAXS pattern of MSU-S$_{ZSM5}$, and (b) XRD pattern of HZSM-5 and MSU-S$_{ZSM-5}$.

From Figure 5.1 (a), the SAXS pattern of MSU-S$_{ZSM-5}$ exhibits a strong peak at [100], which confirms the existence of mesostructure of MSU-S$_{ZSM-5}$. However, the two peaks at [110] and [200] are unclearly separated from one another because the presence of aluminum causes a local distortion, and leads to less order structure of MSU-S_{ZSM-5} (Lourenço *et al.*, 2006). Figure 5.1 (b) exhibits that the characteristic peaks of HZSM-5 zeolite are located at 7.94°, 8.89°, 14.77°, and 23.96°. Although MSU-S_{ZSM-5} has a broad reflection at about 23°, but it corresponds to the diffraction peak of HZSM-5 (Park *et al.*, 2011). The result from XRF shows that MSU-S_{ZSM-5} has the Si/Al_2 ratio of 39.6.

Next, Table 5.2 illustrates the surface area, pore volume, and pore size of HZSM-5 and MSU-S_{ZSM-5}. The result shows that the N_2 adsorption-desorption isotherm of MSU-S_{ZSM-5} show the sudden step at 0.35 which is the same as Al-MCM-41 (Triantafyllidis *et al.*, 2007). Furthermore, H.K. and B.J.H methods are used to identify the micropore and mesopore diameter. MSU-S_{ZSM-5} provides mesopore diameter around 2.86 nm and gives 3 times higher surface area than microporous HZSM-5.

Table 5.2 Physical properties of HZSM-5 and MSU-S_{ZSM-5}

Catalysts	**Surface Area (m^2/g)** [a]	**Pore Volume (cm^3/g)** [b]	**Micropore Diameter (Å)**[b]	**Mesopore Diameter (Å)**[c]
HZSM-5	361.6	0.312	7.07	-
MSU-S_{ZSM-5}	1,028	1.02	7.10	29.6

[a] Determined by BET method
[b] Determined by H.K. method
[c] Determined by B.J.H. method

5.4.2 The Activity of MSU-S_{ZSM-5} on Bio-ethanol Dehydration

For the dehydration of bio-ethanol, MSU-S_{ZSM-5} gives almost 100 % ethanol conversion through 96 hours time-on-stream. Figure 5.2 (a) exhibits the concentration profiles of gaseous products from MSU-S_{ZSM-5} with TOS. The large pore size of MSU-S_{ZSM-5} tends to produce a high gaseous yield with a low oil yield. Ethylene was almost the only component in the gas stream after 24 hours TOS. However, for the petroleum fractions of MSU-S_{ZSM-5}, with increasing TOS, gas oil fraction tends to decrease adversely with kerosene fraction. Because the acid sites are poisoned by coke; so, the poisoning decreases the amount of gas oil fraction as shown in Figure 5.2 (b).

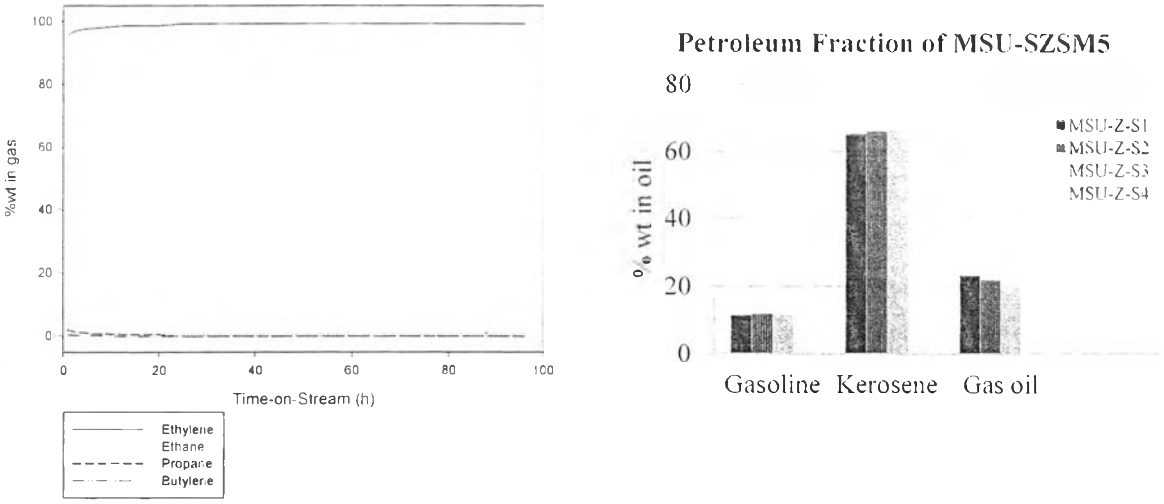

Figure 5.2 (a) Concentration profile of gaseous products obtained from MSU-S_{ZSM-5}, and (b) Petroleum fraction of oil MSU-S_{ZSM-5} (S1, S2, S3, S4 = 24, 48, 72, and 96 hours TOS).

According to Figure 5.3, the catalyst still has the potential to transform bio-ethanol into hydrocarbons throughout 96 hours time-on-stream. For the oil composition, C_{10+} aromatic group is the main fraction in oil, followed by C_9 aromatics, benzene, and xylenes, accordingly. Furthermore, the C_9 aromatics, benzene, and xylenes selectivities tend to increase adversely with C_{10+} aromatics selectivity that decreases with time-on-stream. Polyaromatic hydrocarbons can be formed in the large pore size of MSU-S_{ZSM-5}, and some of those molecules can be deposited on the acid sites of the catalyst, which causes coking (Madeira *et al.*, 2009). Moreover, Brønsted acid sites has the important role to the formation of C_{10+} hydrocarbons (Ramasamy and Wang, 2014) but the acid sites are poisoned by the coke; so, it can be confirmed by the decline of C_{10+} aromatics as shown in Figure 5.3.

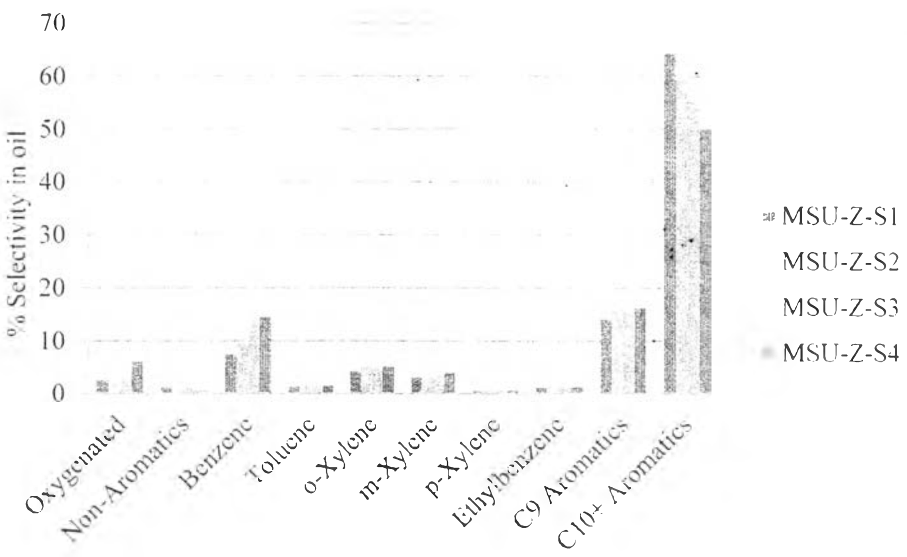

Figure 5.3 Oil compositions from MSU-S_{ZSM-5} along with TOS.

5.5 Conclusion

The hierarchical mesoporous MSU-S_{ZSM-5} was successfully synthesized by using TPAOH as a template and CTAB as a surfactant. The characterization from SAX provided the strong peak at [100], which confirms the mesostructure of MSU-S_{ZSM-5}. Moreover, MSU-S_{ZSM-5} exhibited the surface area of 1,028 m^2/g, which is 3 times higher than conventional HZSM-5. The results from bio-ethanol dehydration showed that most of gaseous products was ethylene, and ethylene became the only component after 24 hours time-on-stream. For the oil composition, C_{10+} aromatic group was the main fraction in oil, followed by C_9 aromatics, benzene, and xylenes, accordingly. Furthermore, C_9 aromatics, benzene, and xylenes selectivities tended to increase adversely with C_{10+} aromatics selectivity, decreasing with time-on-stream.

5.6 Acknowledgements

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5.7 References

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