CHAPTER VIII

ENHANCING SELECTIVITY OF MIXED XYLENES FROM BIO-ETHANOL DEHYDRATION FROM USING THE TWO CONSECUTIVE LAYERS OF MICROPOROUS HZSM-5 OR HBETA CATALYSTS AND THEIR HIERARCHICAL MESOPOROUS MATERIALS.

8.1 Abstract

The two consecutive layers of a microporous catalyst and a mesoporous material with the same microporous seed were studied, aiming to transform bio-ethanol into more heavy liquid hydrocarbons. The first layer was filled with either microporous zeolites HZSM-5 or HBeta whereas the second layer was filled with a hierarchical mesoporous MSU-S with either corresponding ZSM-5 or Beta seeds. The results illustrated that both of the two consecutive layers of catalysts with the ZSM-5 and Beta seed cannot increase either the oil yield or the larger hydrocarbons compared to the single layer of HZSM-5 and HBeta. Furthermore, the additional second layer can promote the dealkylation and transalkylation of large hydrocarbon molecules such as C_9 and C_{10+} aromatic into petrochemical products such as mixed xylenes. Moreover, both of the two consecutive layers from different seed type gave a higher ratio of BTEX/Oil, BTEX/Aromatics, and xylenes/BTEX than the single layer of their microporous seed types. Additionally, both of MSU-S_{ZSM-5} and MSU-S_{BEA} at the second layer selectively produced m-xylene.

8.2 Introduction

The decrement of petroleum source is the one of world's energy problems. Lacking of petroleum reserve drives the world to find another alternative source of energy. Bio-ethanol is one of the alternative sources that has many advantages such as reduce greenhouse gases. Purified bio-ethanol can be blended with gasoline to produce gasohol E10, E20, and E85 for uses in the vehicles. Moreover, petrochemical compounds such as BTEX are very high valuable products. One of the best known is p-xylene which is the raw material for manufacturing fibers and films, and the most important product is polyethylene terephthalate (PET).

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). Park and Seo (2009) studied methanol to olefins reaction over several zeolites using CHA, LTA, MFI, BEA, MOR, and FAU. They found that BEA, MFI, and FAU were selectively produce C_{5+} and alkylaromatics. 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; however, 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 salt 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_{ZSM-5}) and Beta (MSU-S_{BEA}) seeds which were the composite of MCM-41 and ZSM-5 and Beta zeolite. 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 the Si/Al_2 ratio of 81 possessed the large pore size of about 2.72 nm and the 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 aromatics and xylenes. Moreover, methanol dehydration 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 the 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 two consecutive layers of catalysts were studied on the purpose of increasing the amount of heavy liquid hydrocarbon from the catalytic dehydration of bio-ethanol. The first layer was filled by a commercial microporous zeolite; that is, H-Beta or HZSM-5 with Si/Al_2 ratio of 37 and 30, in order to produce some hydrocarbon compounds. Then, hydrocarbons from the first layer will be preferably further reacted in the hierarchical mesoporous MSU-S, which have a bigger pore size, so that heavy liquid hydrocarbons such as kerosene and gas oil can be further produced in a large amount. The reaction was performed at 450 °C under atmospheric pressure for 8 hours.

8.3 Experimental

8.3.1 Catalyst Preparation

8.3.1.1 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, respectively 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.

8.3.1.2 Synthesis of MSU-S_{BEA}

To prepare the BEA-seed solution, a mixture of Al-(i-BuO)$_3$ (0.02 mol) and TEOS (0.98 mol) were added to a stirred solution of aqueous TEAOH (35 wt%, 0.37 mol) in H_2O (20 mol). After aging about 2 hours, the solution was transferred into a Teflon-line autoclave and hydrothermal treatment at 100 °C for 3 hours to form BEA-seeds. After that, the seed solutions was added to a solution of CTAB (0.25 mol) in H_2O (127 mol). The solution was adjusted to a pH 9.0 by sulfuric acid (0.17 mol). The resulting synthesis gel was hydrothermally treated in a Teflon-lined autoclave at 150 °C for 2 days to form the mesostructure The solution was filterd, washed, dried, and calcined at 2 °C/min to 550 °C for 4 hours to obtain the MSU-S_{BEA} catalysts (Liu *et al.*, 2001; Triantafyllidis *et al.*, 2007).

8.3.1.3 Commercial Zeolites

HZSM-5 zeolite (MFI, NH_4-form, SiO_2/Al_2O_3 = 30 mol/mol, BET surface area = 340 m^2/g, Zeolyst International, USA), and HBeta zeolite (BEA, NH_4-form, SiO_2/Al_2O_3 = 37 mol/mol, BET surface area = 502 m^2/g, Zeolyst International, USA) were calcined at 500 °C, 10 °C/min for 4 hours, and 550 °C, 2 °C/min for 6 hours to get the H-form zeolite. Then, they were pelletized, crushed, and sieved to 20-40 meshes before use in the reactor. The abbreviations of catalysts used in the experiment are shown in Table 8.1

8.3.2 Catalyst Characterization

The surface area (BET), pore volume (Horvath Kawazoe method), and pore size (Barret-Joyner-Halenda method) were determined based on N_2 physisorption using the Thermo Finnigan/Sorptomatic 1990. Rigaku TTRAX III was used in the small-angle mode to determine the Small Angle X-Ray Scattering (SAXS) pattern of MSU-S_{BEA} from 1°-7° with scan speed of 1°/min. For the wideangled, Rigaku Smartlab® was use to determine from 5°-50° with the scan speed of 5°/min with the increment of 0.01. The Si/Al ratio of the synthesized MSU-S_{BEA} and MSU-S_{ZSM-5} was determined by XRF.

Table 8.1 Nomenclature of catalysts used in the experiments

# of run	Catalyst	Abbreviation
1	HZSM-5	HZ
2	HZSM-5 in the first layer and MSU-S_{ZSM-5} in the second layer	HZ:MSU-Z
3	HBeta	HB
4	HBeta in the first layer and MSU-S_{BEA} in the second layer	HB:MSU-B

8.3.3 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 layer reactor under atmospheric pressure at 450 °C for 8 hours. The first layer was filled with 1.5 g of HBeta or HZSM-5 and cover with glass wool then, 1.5 g of a hierarchical mesoporous MSU-S with corresponding either Beta or ZSM-5 seed was place in the second layer. 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.

8.4 Results and Discussion

8.4.1 Catalyst Characterization

Rigaku TTRAX III was used in the small-angle mode to determine the Small Angle X-Ray Scattering (SAXS) pattern of MSU-S_{BEA} from 1^{o}-7^{o} with scan speed of 1^{o}/min. For the wide-angles, Rigaku Smartlab® was used to determine from 5^{o}-50^{o} with the scan speed of 5^{o}/min. The results from SAXS show that both MSU-S_{ZSM-5} and MSU-S_{BEA} exhibit a strong peak at [100], but two peaks at [110] and [200] unclearly separate because the presence of aluminum causes a local distortion, and leads to less order structure of MSU-S_{BEA} (Lourenço *et al.*, 2006) indicating a non-uniform hexagonal structure (Schwanke *et al.*, 2013) as shown in Figure 8.2 (a) and (c). Moreover, Figure 8.1 (b) and (d) illustrate the wide-angle mode XRD patterns of HZSM-5 with MSU-S_{ZSM-5} and HBeta with MSU-S_{BEA}, respectively. The characteristic peaks of HBeta zeolite are located at 8.11^{o} and 22.82^{o} whereas those of HZSM-5 zeolite are located at 8.27°, 9.17°, 23.57°, 24.04° and 24.24°. Although both MSU-S_{ZSM-5} and MSU-S_{BEA} have a broad reflection at about 22^{o}-23^{o}, but they can also be contributed from the diffraction peaks of HZSM-5 and HBeta (Park *et al.*, 2011). The results from XRF show that MSU-S_{ZSM-5} and MSU-S_{BEA} have the Si/Al_2 ratio of 39.6 and 75.6, respectively.

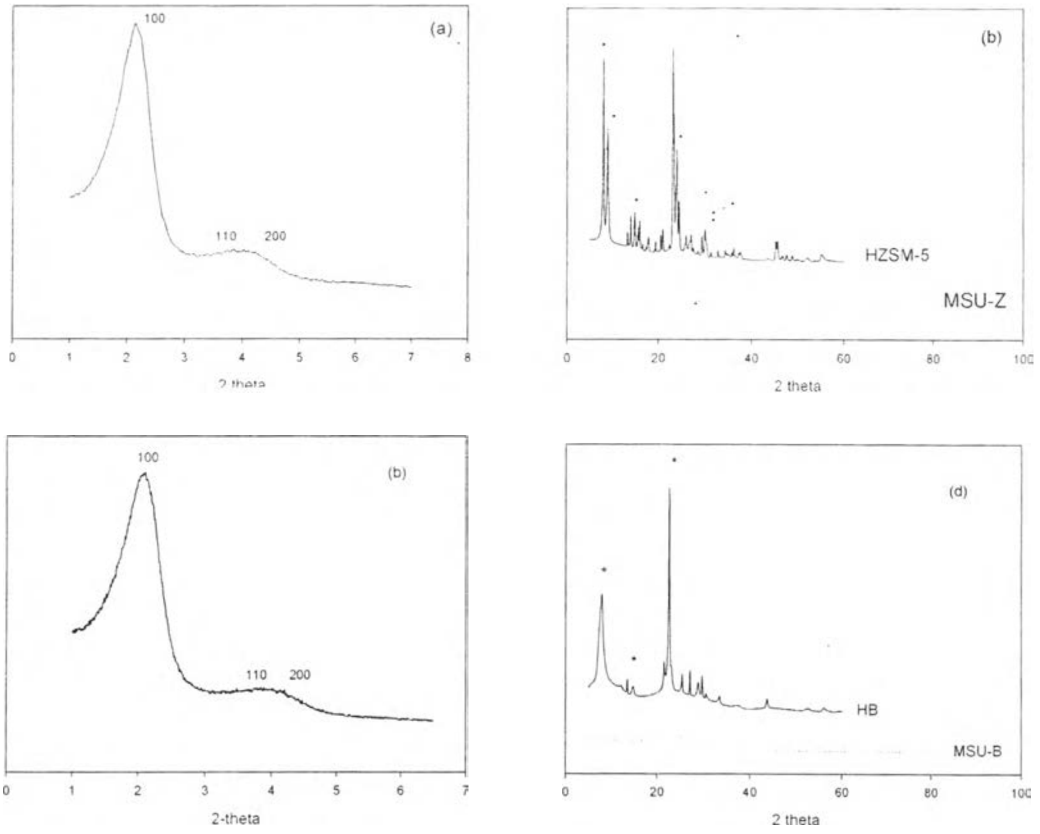


Figure 8.1 SAXS pattern of (a) MSU-S_{ZSM5} and (b) MSU-S_{BEA}, and XRD pattern of (c) HZSM-5 with MSU-S_{ZSM5}, and (d) HBeta with MSU-S_{BEA}.

Next, Table 8.2 illustrates the surface area, pore size and pore volume of the hierarchical mesoporous MSU-S materials with Beta and ZSM-5 seeds as compared to their corresponding microporous zeolites. It can be seen that both MSU-S_{ZSM5} and MSU-S_{BEA} exhibit higher surface area, pore volume, and pore size than their corresponding microporous zeolite seeds.

Table 8.2 Physical properties of HBeta, HZSM-5, MSU-S_{BEA}, and MSU-S_{ZSM-5}

Catalysts	**Surface Area (m^2/g)** [a]	**Pore Volume (cm^3/g)** [b]	**Micropore Diameter (A)**[b]	**Mesopore Diameter (Å)**[c]
HBeta	502.3	0.26	7.93	-
HZSM-5	361	0.159	5.97	-
MSU-S_{BEA}	855.4	1.20	7.7	29.0
MSU-S_{ZSM-5}	1,028	1.02	8.97	28.66

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

8.4.2 Consecutive Layers of HZSM-5 and MSU-S_{ZSM-5}

For the dehydration of bio-ethanol, HZ:MSU-Z exhibits high ethanol conversion of about 99.2 %, which is insignificantly different from that of the single layer of HZ. The additional second layer does not give a higher either oil yield or heavier hydrocarbons, as compared to the single layer of HZ. Moreover, the composition of oil from HZ:MSU-Z is illustrated in Figure 8.2. The selectivity of C_9 and $C10^+$ aromatic fractions is suppressed with using HZ:MSU-Z catalysts because the MSU-S_{ZSM-5} in the second layer can promote the transalkylation and dealkylation reaction of C_9 and C_{10+} aromatics into toluene, and mixed xylenes, resulting in the increase in gasoline fraction from 81 % to 89 %wt as shown in Figure 8.3. Additionally, Figure 8.4 shows that o-xylene and m-xylene are selectively produced by the additional second layer of MSU-S_{ZSM-5}.

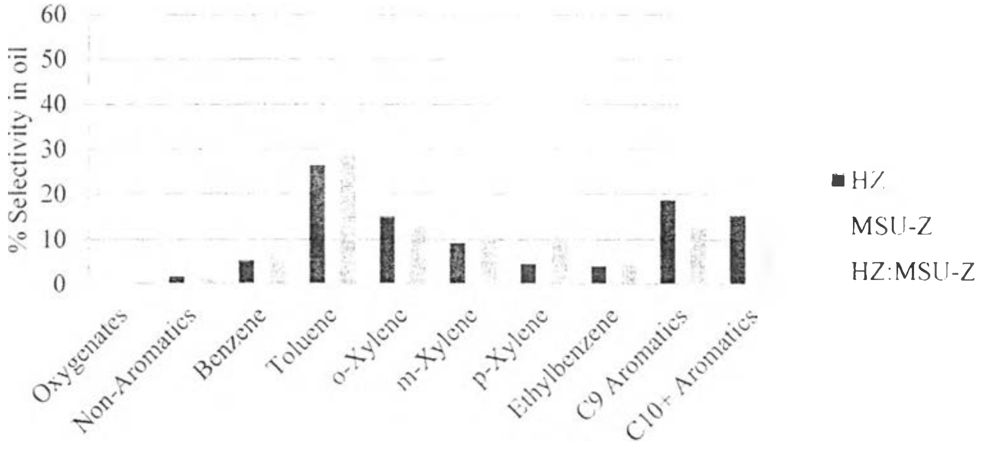


Figure 8.2 Oil compositions from using a single layer of HZ, MSU-Z, and consecutive layers of HZ:MSU-Z.

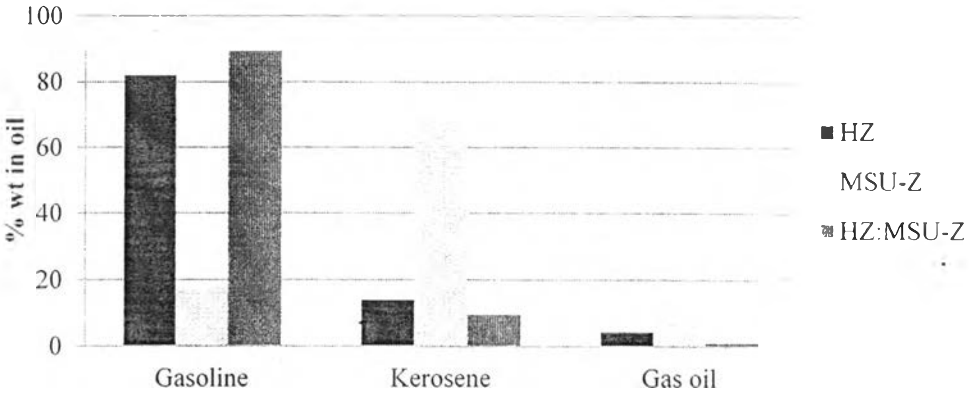


Figure 8.3 Petroleum fractions from using a single layer of HZ, MSU-Z, and consecutive layers of HZ:MSU-Z.

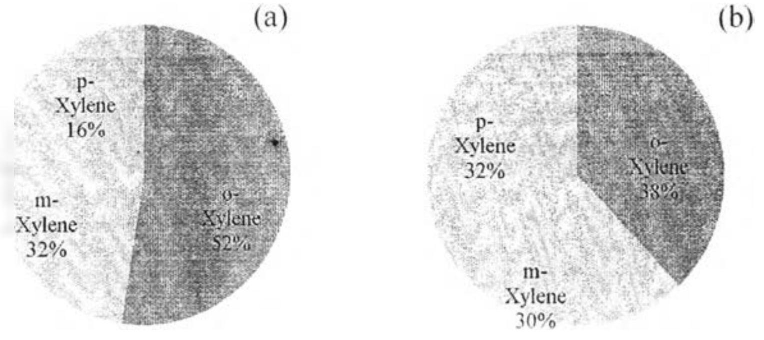
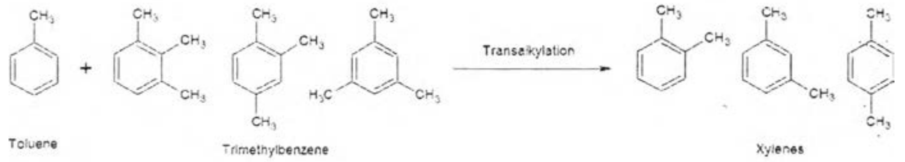


Figure 8.4 Mixed xylenes from using (a) HZ and (b) the consecutive layers of HZ:MSU-Z.

Furthermore, Figure 8.5 displays the ratios of BTEX/Oil, BTEX/Aromatics, and xylenes/BTEX in the oil from using HZ:MSU-Z and HZ. The results show that HZ:MSU-Z gives a higher ratio of BTEX/Oil, BTEX/Aromatics, and xylenes/BTEX than that of single layer of HZSM-5. Moreover, most of oil components are produced by the aromatization of higher olefins from HZSM-5, and then, these hydrocarbons should be further grown into the larger molecules in the large pore of MSU-S_{ZSM-5}. However, MSU-S_{ZSM-5} in the second layer cannot produced more heavy hydrocarbons, Shen *et al.* (2009) stated that the catalytic performances of the catalysts are considerably influenced by the acidity and specific surface area. Nevertheless, it promotes the dealkylation and transalkylation reaction of C_9 and C_{10+} atomatics into mixed xylenes. Additionally, the dealkylation and transalkylation reaction of C_{9+} aromatics are shown in the Equations 8.1 and 8.2 below.



(8.1)

(8.2)

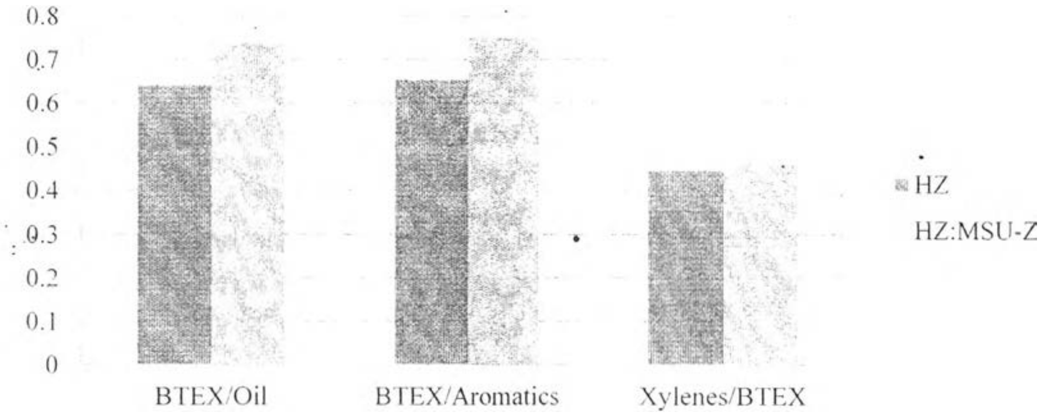


Figure 8.5 Ratios of BTEX/Oil, BTEX/Aromatics, and xylenes/BTEX in oil from using consecutive layers of HZ:MSU-Z and a single layer of HZ.

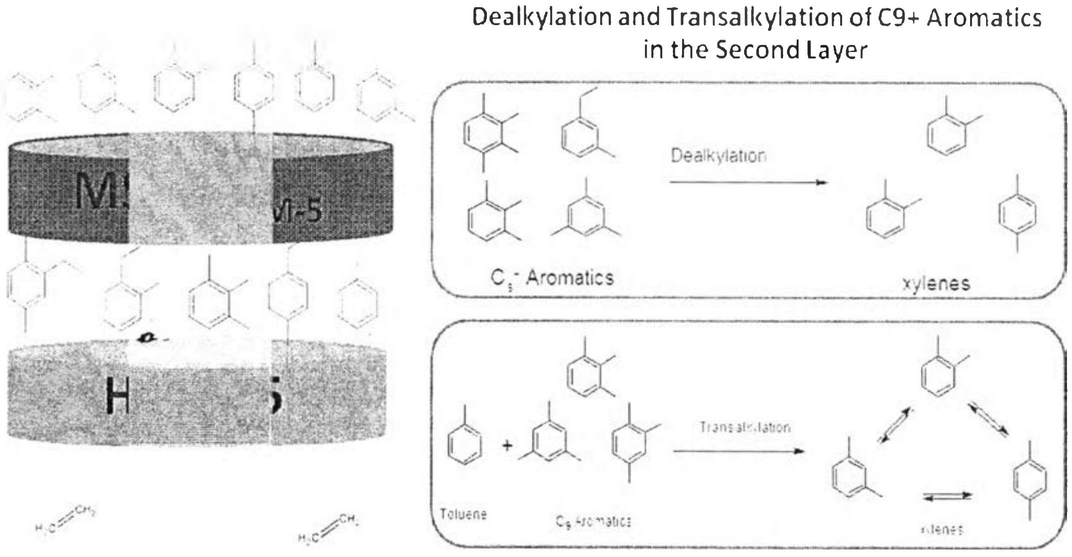
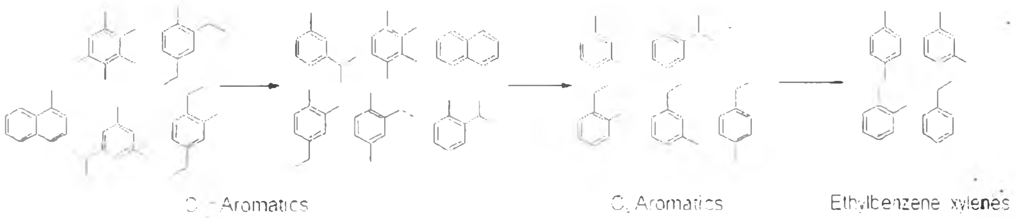


Figure 8.6 Hydrocarbons production using the two consecutive layers of HZSM-5 and MSU-S_{ZSM-5}.

Finally, it can be concluded from Figure 8.6 that when bio-ethanol was dehydrated to ethylene, and then when ethylene passes through HZSM-5 at the first layer, it was transformed to some monoaromatics such as toluene, mixed xylenes, ethylbenzene, C_9, and C_{10+} aromatics. Then, these molecules passed through MSU-S_{ZSM-5} at the second layer, which has a larger pore size for the further formation of larger hydrocarbons. However, MSU-S_{ZSM-5} at the second layer cannot produce larger hydrocarbon, but it promotes the dealkylation, and transalkylation of C_{9+} aromatics into smaller molecules such as toluene, and mixed xylenes.

8.4.3 Consecutive Layers of HBeta and MSU-S_{BEA}

The consecutive double layer of HBeta and MSU-S_{BEA} also provides a high bio-ethanol conversion about 99.5 %, which is insignificantly different from that of the single layer of HBeta. HB:MSU-B neither give a higher oil yield nor heavier hydrocarbons than that of single layer of HB. Furthermore, the composition of oil from HB:MSU-B exhibits a lower selectivity of C_{10+} aromatics, conversely with C_9 aromatics and mixed xylenes selectivity, as shown in Figure 8.7. The decrement of C_{10+} aromatics also results in the decrease amount of gas oil fraction that decrease from 28 % to 15 %, as shown in Figure 8.8. Furthermore, Figure 8.9 illustrates that HB:MSU-B gives a higher ratio of BTEX/Oil, BTEX/Aromatics than that of single layer of HB, but lower xylenes/BTEX. In addition, Figure 8.10 shows that o-xylene is also selectively produced by MSU-S_{BEA} in the second layer. When bio-ethanol was dehydrated to ethylene that next passed through the microporous HBeta. Subsequently, ethylene was transformed into monoaromatic hydrocarbons, especially mixed xylenes, C_9, and C_{10+} aromatics via aromatization of higher olefins. However, when these hydrocarbons pass through the MSU-S_{BEA} in the second layer, they cannot grow into the larger hydrocarbons as the expectation. The explanation might be the same as the previous section that the catalytic performance of the catalyst strongly depends on specific surface area and acidity (Shen *et al.*, 2009) so, C_{10+} aromatics can be undergo dealkylation reaction into the smaller molecules such as C_9 aromatics and mixed xylenes. Additionally, the dealkylation of C_{10+} aromatics into C_9 and mixed xylenes is shown in the Equation 8.3 below.



(8.3)

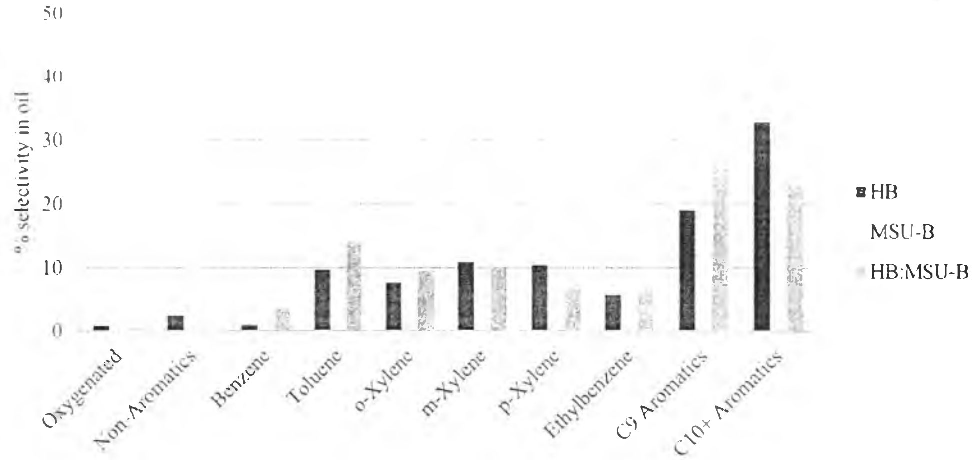


Figure 8.7 Oil compositions from using a single layer of HB, MSU-B, and consecutive layers of HB:MSU-B.

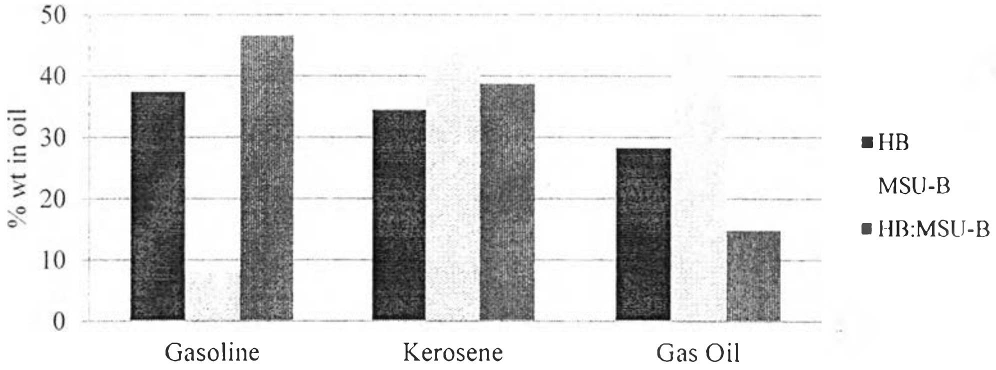


Figure 8.8 Petroleum fractions from using a single layer of HB, MSU-B, and consecutive layers of HZ:MSU-B.

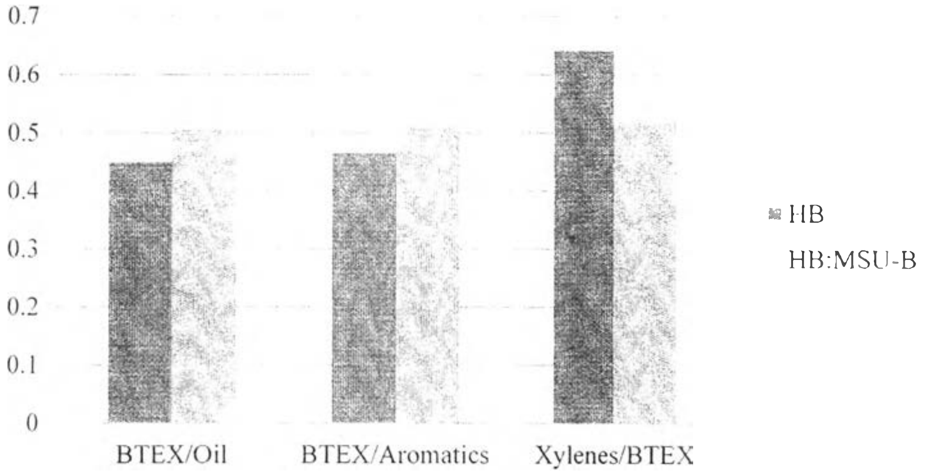


Figure 8.9 Ratios of BTEX/Oil, BTEX/Aromatics, and xylenes/BTEX in oil from using consecutive layers of HB:MSU-B and a single layer of HB.

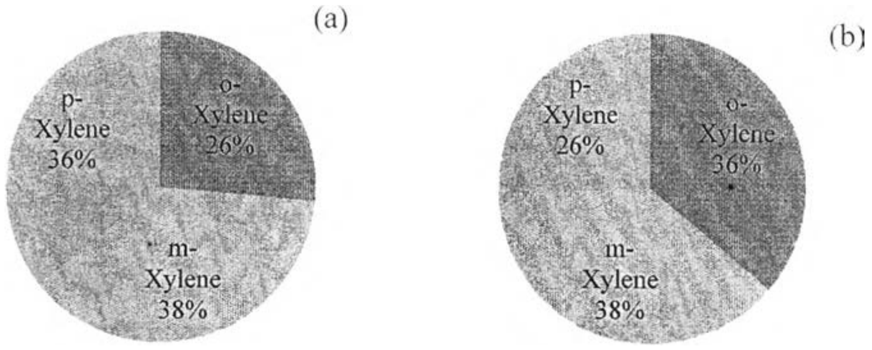


Figure 8.10 Mixed xylenes from using (a) HB and (b) the consecutive layers of HB:MSU-B.

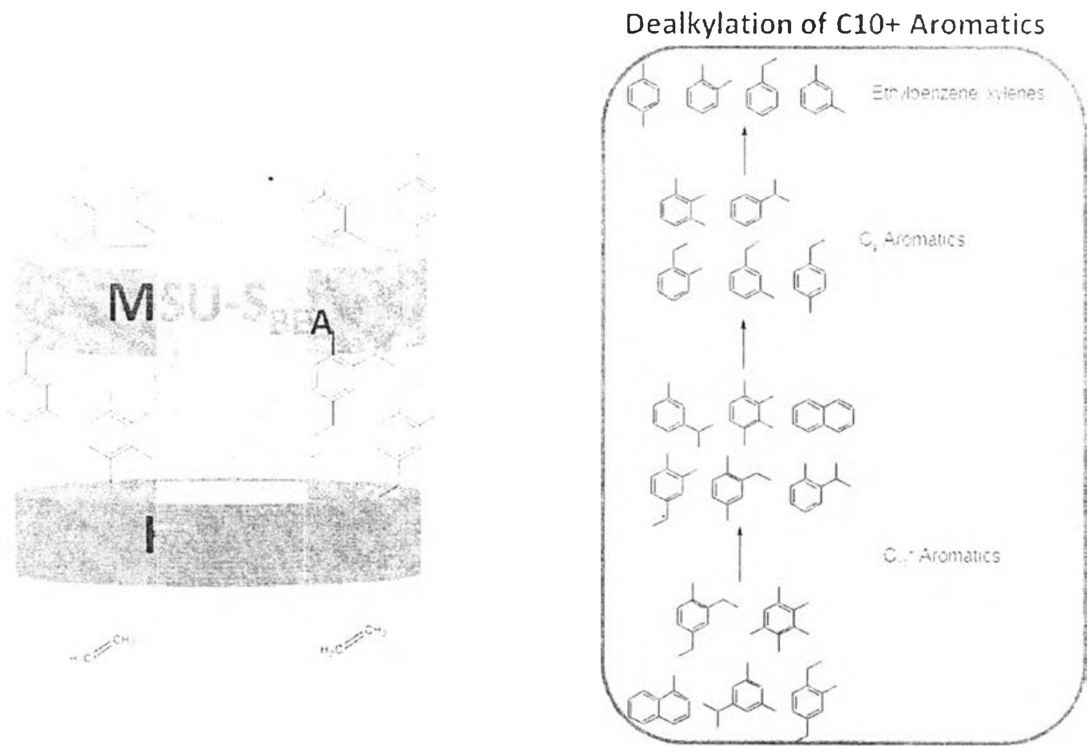


Figure 8.11 Hydrocarbons production using two consecutive layers of HBeta and MSU-S_{BEA}.

So, it can be concluded that when bio-ethanol is dehydrated to ethylene, and then when ethylene passes through HBeta at the first layer, it is transformed into some monoaromatics such as C_9 and C_{10+} aromatics due to its large pore size with a strong acidity, followed by mixed xylenes, toluene, accordingly. Then, when hydrocarbons from the first layer pass through MSU-S_{BEA} at the second layer, the large hydrocarbons such as C_{10+} aromatics are dealkylated in the second layer into the smaller molecules such as C_9 aromatics, toluene, and mixed xylenes as shown in Figure 8.11.

8.5 Conclusions

In this work, the synthesized hierarchical mesoporous MSU-S_{BEA} and MSU-S_{ZSM-5} were placed in the second layer whereas their corresponding microporous zeolite was placed in the first layer. Both HZ:MSU-Z, and HB:MSU-B gave no significant difference on bio-ethanol conversion, compared to those of HB, and HZ. Moreover, the introduction of MSU-S_{BEA} and MSU-S_{ZSM-5} in the second layer neither produced more oil yield nor heavier oil fraction. The selectivity of $C10^+$ aromatics decreased with the presence of the catalyst in the second layer due to the MSU-S_{BEA}, and MSU-S_{ZSM-5} in the second layer promoted the dealkylation and transalkylation reaction, which also resulted in the increase of lighter oil fraction such as gasoline and kerosene. It can be explained that the catalytic performance of the catalyst was strongly affected by the acidity and specific surface area. Furthermore, both HZ:MSU-Z, and HB:MSU-B also gave a higher ratio of BTEX/Oil, BTEX/Aromatics, and xylenes/BTEX than those of HB, and HZ. As a result, mixed xylenes and toluene were selectively produced by both MSU-S_{BEA} and MSU-S_{ZSM-5} in the second layer.

8.6 Acknowledgements

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8.7 References

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