

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

In this work, the influences of time-on-stream (TOS) on the product distribution of microporous zeolites and their hierarchical mesoporous materials, and the effect on the addition of the hierarchical mesoporous materials in the second layer on producing large hydrocarbon molecules, were studied in bio-ethanol dehydration.

The hierarchical mesoporous MSU-S with Beta and ZSM-5 seeds were successfully synthesized by using TEOH, and TPAOH as a structure directing template, respectively, and using CTAB as a surfactant. Moreover, the results from varied TOS in bio-ethanol dehydration of HZSM-5 showed the decrement in propane selectivity in the opposite way with ethylene, propylene, and mixed C₄ due to the deactivation of Brønsted acid site, needed for the hydrogen transfer reaction, whereas MSU-S_{ZSM-5} exhibited high ethylene selectivity along TOS. Furthermore, the oil compositions from HZSM-5 still gave heavier fractions such as C₉ and C₁₀₊ aromatics, resulting in the increasing amount of kerosene fraction whereas C₁₀₊ aromatics selectivity from MSU-S_{ZSM-5} decreased with increasing TOS because the coke deposition in the mesopore of MSU-S_{ZSM-5} can prevent the further reaction of ethylene to higher hydrocarbons, resulting in the decrease of gas oil fraction. In addition, HZSM-5 provided a lower amount of coke deposition because the polyaromatics cannot be formed in its moderate pore size. The structure HZSM-5 and MSU-S_{ZSM-5} were not destroyed during bio-ethanol dehydration, but MSU-S_{ZSM-5} began to be dealuminated after 3 days TOS. On the other hand, the ethylene selectivity of HBeta rapidly increased after 8 hours TOS due to the deactivation of strong acid sites whereas for MSU-S_{BEA}, ethylene was the majority along TOS. Moreover, p-xylene and C₁₀₊ aromatic fraction in the oil from HBeta tended to decrease because polyaromatics can be condensed in the pore of HBeta, which caused coking. Furthermore, MSU-S_{BEA} provided the high selectivity of non-aromatic fraction that was mostly composed of C₁₆ olefins, which tended to

transform into C_9 and C_{10+} aromatic fractions via aromatization with increasing TOS. Although the structure of HBeta was not destroyed during bio-ethanol dehydration, but it was fully deposited by coke after 1 day TOS and began to be dealuminated after 3 days TOS whereas MSU-S_{BEA} still had high surface area and pore volume with no dealumination after 3 days TOS.

Furthermore, the results from the two consecutive layers of microporous HBeta or HZSM-5 zeolite and the hierarchical mesoporous MSU-S with corresponding either Beta or ZSM-5 seeds showed that both of the additional second layer of MSU-S_{ZSM-5} and MSU-S_{BEA} neither produced more oil yield nor heavier oil fractions. Moreover, MSU-S_{ZSM-5} and MSU-S_{BEA} promoted the dealkylation and transalkylation of large hydrocarbons produced from the first layer of HZSM-5 or HBeta such as C_9 and C_{10+} aromatics into mixed xylenes, resulting in the increase of lighter fraction of oil such as gasoline and kerosene. Additionally, both of the two consecutive layers of catalysts also gave a higher ratio of BTEX/Oil, BTEX/Aromatics, and xylenes/BTEX than the single layer and selectively produced toluene and xylenes.

9.2 Recommendations

According to the results, it can be noticed that in case of producing more non-aromatic fraction, mostly composed of olefins and alkanes, the important parameters are time-on-stream, pore size, and acidity. So, further investigation should be conducted in the optimum condition for the proper acidity, and time-on-stream by using mesoporous catalysts with a large pore size, which can enhance the diffusion of large molecules.