

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

In this work, the attempt to convert alternative resources, glycerol and palm fatty acid distilled (PFAD) to aromatics was achieved over Zn/HZSM-5 catalysts. The roles of each Zn species in the aromatization activity were explored. Among the conventional Zn species; the exchangeable Zn^{2+} , $(\text{ZnOH})^+$, and ZnO, $(\text{ZnOH})^+$ species performed the best in the transformation of glycerol to aromatics. The selectivity of aromatics significantly increased with the decrease of light paraffins. The result confirmed the high ability in dehydrogenation of this Zn species. However, using PFAD as a feedstock gave a different conclusion. The result showed that the catalyst, containing small amount of ZnO incorporating with $(\text{ZnOH})^+$ species remarkably improved the transformation of PFAD to aromatics. From product distributions, we concluded that the ZnO played a key role in decarboxylation of fatty acid, generating CO_2 . The shifting from decarbonylation of PFAD on Brønsted acid site to decarboxylation on ZnO resulted in preserving the Brønsted acid site for aromatization. The resulted long chain hydrocarbon was further cracked over Brønsted acid site and passed through the aromatization reaction which $(\text{ZnOH})^+$ species and Brønsted acid site takes responsibility.

To further understand the active site of Zn/HZSM-5 catalyst, we explored the evolution of Zn species by using the thermal treatment under inert or hydrogen atmosphere. The XPS showed that by using aqueous phase ion-exchange method, only $(\text{ZnOH})^+$ species was found in as-prepared Zn/HZSM-5 catalyst. Under the reaction temperature, most of Zn species stabilized in the form of isolated $(\text{ZnOH})^+$ while a minor part of $(\text{ZnOH})^+$ combined with the neighboring hydroxyl group and created the exchangeable Zn^{2+} species. The conventional $(\text{ZnOH})^+$ showed the improvement in aromatization of *n*-pentane as agreed with our previous work. Nonetheless by introducing the hydrogen treatment, the hydrodehydroxylation of $(\text{ZnOH})^+$ generated the new active $(\text{ZnH})^+$ and $(\text{ZnH}_3)^+$ species. The remarkable increase in aromatics selectivity was noticed, illustrating the higher aromatization

activity of $(\text{ZnH})^+$ and $(\text{ZnH}_3)^+$ species, as compared with the conventional $(\text{ZnOH})^+$ species. However, under the absence of H_2 , the most active species, $(\text{ZnH}_3)^+$, decomposed to $(\text{ZnH})^+$, resulting in a somewhat lower the aromatization activity. Even though the $(\text{ZnH}_3)^+$ was unstable in the absence of H_2 , it could be reproduced upon H_2 treatment.

The last part of this work dedicated to the designing of catalyst that provided both high selective of *p*-xylene and high catalytic activity. ZnHZSM-5 catalyst was used as a core, coated with silicalite-1 layer to suppress the isomerization of *p*-xylene. Even the *p*-xylene selectivity was increased; the decrease of Brønsted acidity also lowered the aromatics yield. With the aim to improve catalytic activity while preserving *p*-xylene selectivity, the Sil-1/ZnHZSM-5 catalyst was later grafted with Zn cations by using strong electrostatic adsorption method. The XPS confirmed the formation Zn(II)ions on silicalite-1 layer, clearly differentiated from $(\text{ZnOH})^+$ species. The high performance in dehydrogenation was found over this Zn species, thus aromatics yield was significantly improved over Zn(II)ions/Sil-1/ZnHZSM-5 catalyst. The results indicated that Zn(II)ions on silicalite-1 play a role in converting *n*-pentane to olefins. Whereas, $(\text{ZnOH})^+$ in ZnHZSM-5 catalyst performed the aromatization of resulted olefins.

8.2 Recommendations

Even the roles of Zn species on Zn/HZSM-5 catalyst have been studied for decade, this topic still be a matter of dispute. In this work we proposed the effects of each Zn species based on our experimental results and previous theoretical investigations. However we accepted that there is only a few works studied on the effects of hydrogen on the evolution of Zn species. Thus, we strongly recommended the further study to do the theoretical investigation, DFT, to explain the mechanism of $(\text{ZnH})^+$ and $(\text{ZnH}_3)^+$ species in improving aromatization reaction.

Focusing on the modified Zn/HZSM-5 catalyst for highly selective *p*-xylene formation, approximately 50 % of *p*-xylene selectivity in xylenes was achieved, implying that only partially external Brønsted acid sites were covered by silicalite-1

layer. To improve the *p*-xylene selectivity, two cycle of depositing silicalite-1 was recommended. Nonetheless, it should be concerned that a deposition of too thick silicalite-1 layer also causes a reduction of catalyst activity, mechanical strength, compactness of the silicalite-1 layer. In the beginning, the studied on synthesis method of a very thin layer without defect should be a target of the study.