

CHAPTER X

CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

Conversion of methane into chemicals or liquid fuels is currently an interesting topic and will become more attractive in the near future, as a result of tighten supplies of crude oil. Due to an abundance of methane (predominantly in natural gas resources), widening exploitation of methane, for example methane-to-liquids, methane-to-methanol, methane-to-aromatics, and etc., has been being conducted, especially for the last decade. Moreover, a more stringent environmental legislation is also one of the key driving forces for this research area. The present work demonstrated 2 aspects of methane utilization. One is a novel reaction (benzene methylation reaction) attempting to utilize methane as an alkylating species to methylate benzene into higher-valued aromatics (i.e., xylenes). Another is a conventional approach (Fischer-Tropsch reaction), which indirectly uses methane through synthesis gas, a gas mixture of CO and H₂ derived from methane. Although this technology has been in a commercial scale, there are lots of issues emerged, which are needed to be solved to improve the process efficiency. This work coped with the improvement of Co-based Fischer-Tropsch catalyst using metal promoters and the investigation of catalyst deactivation at the onset of Fischer-Tropsch reaction.

Ag/HZSM-5 and Mo/HZSM-5 catalysts were selected to study for the methylation reaction. Briefly, metal (Ag or Mo) is responsible for activating methane, Brønsted proton (H⁺) is responsible for alkylation reaction, while ZSM-5 with 8 member ring pore size is expected to play a role in *p*-xylene selectivity, if xylenes formed inside the pore. Ag/HZSM-5 is able to catalyze the reaction into xylenes, the desired product, however toluene is a major product and heavy aromatics is also formed. Activation this catalyst under 5% H₂/N₂ at 350 °C is most appropriate conditions, in which a proposed Ag_n^{δ+} (2 ≤ n ≤ 4) active species is generated. Notwithstanding, this active Ag species is susceptible to the reaction conditions, thereby causing it transformed into inactive forms (Ag⁺ and Ag⁰) and

dramatic drop in activity is obtained. Mo/HZSM-5 is also able to promote this reaction but it contributes to the formations of heavy aromatics (predominantly by naphthalene) and toluene without xylenes formation. Heavy aromatics can be successfully minimized with maximizing toluene by co-feeding with H₂. The more the H₂ content, higher the toluene yield but lower the benzene conversion. Most active Mo/HZSM-5 is activated in a flow of pure H₂ at 550 °C, in which metallic Mo is generated and dominates in a catalyst. Despite high activity, metallic Mo is susceptible to the reaction conditions. Oxidation of metallic Mo into oxidized forms is a main cause of catalyst deactivation; moreover, coke formation covered on catalyst surface is also an issue.

Co-based Fischer-Tropsch catalyst, an effective catalyst for conversion of synthesis gas containing high H₂/CO ratio, was studied under the aim at improving its activity, selectivity, and stability. Metal promoter Pt, a most commonly used promoter, and Ag, an alternate promoter, were compared in many relevant aspects, including Co reduction facilitation, local atomic structure, and catalyst performance (e.g., activity, selectivity). Ag showed a satisfied performance as metal promoter and was promoted as a promising substituent for Pt. The ability of metal promoters to maintain their function in facilitating Co oxide reduction after regeneration was initially scanned through the designed method, oxidation-reduction (OR) cycles. Pt, Ag, and other metal promoters (e.g., Ru, Re, Au, Rh, Ir) were brought to study. The result showed that all studied metal promoters can maintain facilitating Co oxide reduction after the OR cycles, even up to 3 cycles, except to Au that can no longer facilitate the reduction, even just after 1 cycle. Typically, cobalt-supported catalysts contain rather high Co loading (10-25 wt%) in order to avoid the oxidation of metallic Co active site during the reaction. On the other hand, due to a high price of Co, there are many research groups affording to use lower Co loading. However, there are many problems emerged, especially catalyst deactivation. This work has explored that small Co crystallite in low Co content catalyst can be oxidized into CoO by the conditions at the onset of Fischer-Tropsch run with 50% CO conversion.

10.2 Recommendations

For methylation work, it was found that to accomplish the reaction between benzene and methane into higher-valued product (e.g., *p*-xylene) with a one step process is quite difficult. Although Ag/HZSM-5 can promote the desired reaction route, its conversion, selectivity, and, even, stability is disappointing. Therefore, a two-step reaction process seems to be more practical. Methane is first converted into more active chemicals such as methyl alcohol or methyl halide. Then, either one of these methane derivative chemicals will be brought to react with benzene to perform the methylation reaction. For the methylation reaction, it is recommended to carry out the reaction in the gas phase using a HZSM-5 based catalyst, as the benefit of *p*-xylene shape selective of ZSM-5 can be utilized.

For Co-based Fischer-Tropsch catalysts, Ag as a metal promoter was advocated, according to the results demonstrated in this work. However, the capability of Ag as metal promoter after catalyst regeneration following the reaction test is required to be examined, so that the ability of Ag to maintain its promoting effect after real catalyst regeneration can be verified. Moreover, cobalt in cobalt-supported catalyst should be in an optimal size, namely not too large to lower the Co site density and not too small to be susceptible to reoxidation, which causes a decrease in active site density.