ABSTRACT

Cyclar process was previously developed to convert propane and butane into aromatics using gallium-promoted ZSM-5 zeolites (Ga/ZSM-5). However, it has two major limitations. Firstly, light gases (methane and ethane) limit the yield of higher molecular weight hydrocarbons for propane conversion. Secondly, ethane is unreactive on Ga/ZSM-5 catalysts. Relative rates and selectivity for propane conversion on two components, gallium (Ga/Al_2O_3) and acid ZSM-5 (H-ZSM-5) were investigated, and the results suggest that light gas was produced by propane monomolecular cracking on ZSM-5 due to the imbalance of alkane dehydrogenation and olefin conversion rates on two catalytic functions. A PtZn alloy catalyst, which has >99% propene selectivity and 30 times higher rate than Ga, was used for the dehydrogenation function. The bifunctional PtZn/SiO_2+ZSM-5 catalyst has high yields of aromatics with low methane selectivity (<5%) at ~70% propane conversion. The results suggest methane can be minimized by utilizing the PtZn alloy and lowering the monomolecular cracking rate by ZSM-5. In addition, PtZn alloy increases aromatics selectivity. Aromatics formation pathway was investigated by studying the rate and selectivity of a model intermediate (cyclohexene) on ZSM-5, PtZn/SiO2 and Ga/Al_2O_3. Benzene is formed at similar rates on Ga/Al_2O_3 and ZSM-5 but cracking of cyclohexene on the latter is two orders of magnitude higher than the benzene formation rate, indicating cracking of cyclic hydrocarbons leads to low aromatization rate on Ga/ZSM-5. The benzene formation rate on the PtZn/SiO_2 is 200 times higher than that on ZSM-5, suggesting aromatics are formed by the metal pathway on PtZn/SiO_2+ZSM-5.

Unlike Ga/ZSM-5 catalysts, PtZn/SiO_2+ZSM-5 catalysts also convert propane to aromatics at low temperature (350°C). The temperature effect on propane dehydroaromatization pathways on the PtZn/SiO_2+ZSM-5 bifunctional catalysts was investigated to develop strategies for propane conversion to valuable liquid hydrocarbons. At high temperature (550°C), high dehydrogenation rates and lower monomolecular cracking rates are required to minimize methane formation, leading to primarily propene and BTX (benzene, toluene, and xylenes). By

recycling propene in the propane conversion range of 30-45%, >80% BTX yields is likely achievable at full recycle. At mid temperature (400-450°C), the product has high selectivity to gasoline-blending hydrocarbons (butanes, C_5^+ hydrocarbons, toluene, and xylenes) at 15-25% propane conversions because dehydrogenation rates are moderately high, and oligomerization is more favored than cracking. At low temperature (350°C), ~25% propane conversion is achieved and has high selectivity (~60%) to butanes, but the propane conversion rates are likely too low to be practical. While methane formation by monomolecular cracking limits liquid yields at high reaction temperature, at mid and low temperatures, hydrogen co-produced at high propane conversions saturates light olefins to make undesired ethane, which becomes major yield-loss reaction on the PtZn/SiO_2+ZSM-5.

Finally, PtZn/SiO_2+ZSM-5 catalysts can convert ethane to C_3^+ and aromatics but the methane selectivity increases rapidly at high ethane conversion. The roles of two catalytic function (Pt-Zn alloy and ZSM-5) in the dehydroaromatization pathways of ethane and propane will be further studied and their product distribution will be compared to have better understandings on the differences in the dominant yield-loss reaction and dehydroaromatization pathways.