Title: Development of catalysts for upgrading ethane and its derivatives to liquid hydrocarbons

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Abstract

The revolution of shale gas motivated the development of catalytically converting light alkanes to liquid hydrocarbons. Ethane as the second most abundant component in shale gas, showed a great potential to be converted to chemical feedstocks or fuels. Ethane dehydroaromatization (EDA) is able to directly convert ethane to valuable aromatics such as benzene, toluene, and xylene (BTX) in a single reactor. A Pt_3Mn/SiO_2 + ZSM-5 bifunctional catalyst was used to investigate the effect of dehydrogenation and the Brønsted acid catalyst ratio, hydrogen partial pressure, and reaction temperature on the product distributions for EDA. Pt_3Mn/SiO_2 + ZSM-5 with a 1/1 weight ratio showed the highest ethane conversion rate and BTX formation rate. Ethylene is initially formed by dehydrogenation by the Pt_3Mn catalyst, which undergoes secondary reactions on ZSM-5, forming C_3+ reaction intermediates. The latter form final products of CH_4 and BTX. At conversions from 15 to 30%, the BTX selectivities are 82–90%. For all bifunctional catalysts, the ethane conversion significantly exceeds the ethane–ethylene equilibrium conversion due to reaction to secondary products. Low H_2 partial pressures did not significantly alter the product selectivity or conversion. However, higher H_2 partial pressures resulted in increased methane and decreased BTX selectivity. The excess hydrogen saturated the olefin intermediates to form alkanes, which produced methane by monomolecular cracking on ZSM-5. With an increasing reaction temperature from 550 °C to 650 °C, the benzene selectivity increased, while the highest BTX selectivity was obtained at 600 to 650 °C.

Utilizing multiple reactors to sequentially convert ethane to higher molecular weight olefins is another upgrade approach. After ethane is catalytically dehydrogenated to ethylene, it can be further converted to longer olefins or fuels. The most widely studied heterogeneous catalysts are Ni^{2+} ions exchanged on Brønsted acid supports, such as zeolites and silica-alumina, MCM-41, etc., resulting in bifunctional catalysts. In the second study, nickel was loaded onto non-acidic supports, SiO_2 and dealuminated BEA, and compared to a bifunctional ion exchanged Ni^{2+} in H-BEA catalyst. The catalysts were characterized by infrared spectroscopy (IR) of adsorbed

pyridine, in situ X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM). Pyridine IR confirmed the absence of Brønsted acid sites for Ni dealuminated BEA zeolite and silica catalysts; while Brønsted acid sites were still present in Ni exchanged H-BEA. In situ XAS and TEM showed that isolated Ni^{2+} ions bonded to the O ions of the silica and dealuminated BEA are the active site for ethylene oligomerization, while nickel oxide clusters have little activity. Both Ni/SiO_2 and Ni/DeAl BEA were active for ethylene oligomerization at temperatures from 175-400°C. While oligomerization is the major primary product, at these reaction temperatures, additional non-oligomer products were produced including ethane, olefin isomers and odd-carbon numbered olefins. These products suggest that Ni^{2+} sites catalyze additional reactions of hydrogen transfer, double bond isomerization and cracking, respectively. These catalysts were also catalytic for olefin hydrogenation at the oligomerization reaction temperature. As a result, the non-acidic catalysts could be regenerated with hydrogen. The Ni/H-BEA catalyst, however, required regeneration in air at high temperature due to the coke formed on Brønsted acid sites.