Support-Enhanced Thermal Oligomerization of Ethylene to Liquid Fuel Hydrocarbons

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Thermal, non-catalytic conversion of light olefins ($C_2^= - C_4^=$) was originally utilized in the production of motor fuels at several U.S. refineries in the 1920-30's. However, the resulting fuels had relatively low-octane number and required harsh operating conditions ($T > 450$ °C, $P > 50$ bar), ultimately leading to its succession by solid acid catalytic processes. Despite the early utilization of the thermal reaction, relatively little is known about the reaction products, kinetics, and initiation pathway under liquid-producing conditions.

In this thesis, thermal ethylene conversion was investigated near the industrial operating conditions, i.e, at temperatures between 320 and 500 °C and ethylene pressures from 1.5 to 43.5 bar. Non-oligomer products such as propylene and/or higher odd carbon products were observed at all reaction temperatures, pressures, and reaction extents. Methane and ethane were minor products (< 1 % each), even at ethylene conversions as high as 74 %. The isomer distributions revealed a preference for linear, terminal C_4 and C_5. The reaction order was found to be 2nd order with a temperature dependent activation energy ranging from 165 to 244 kJ/mol. The importance of diradical species in generating free radicals during a two-phase initiation process was proposed. The reaction chemistry for ethylene, which has only strong, vinyl C-H bonds starkly contrasted propylene, which possesses weaker allylic C-H bonds and showed preference for dimeric C_6 products over C_2-C_8 non-oligomers.

Extending this work further, the thermal oligomerization of ethylene was enhanced using high surface area supports such as silica and alumina, which have not been reported as oligomerization catalysts. Both supports resulted in rate increases compared to the gas phase reaction, however the ethylene conversion rate with alumina was superior to silica by a factor of between 100 and 1,000. Additionally, the alumina evidently confers a catalytic function, resulting in altered product distributions, notably an increase in branched products such as isobutene and isopentenes. The oligomerization chemistry with alumina appears to reflect the involvement of Lewis acid sites rather than traditional Brønsted acid or transition metal catalysis, which operate via carbenium ion and metal-alkyl intermediates, respectively.