GALLIUM LEWIS ACID CATALYSTS FOR HYDROCARBON REACTIONS: FROM OLEFIN OLIGOMERIZATION TO HEXANES HYDROISOMERIZATION AND HYDROCRACKING

Abstract

Wei-Ling Huang

Advised by Prof. Jeff Miller

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Olefin oligomerization is a widely used reaction for upgrading light olefins into higher molecular weight hydrocarbons in the chemical and petroleum industries. With the increased availability of inexpensive alkanes driven by the shale gas boom, this reaction has gained significant attention. This thesis investigates the effect of SiO_2 and Al_2O_3 supports on Ga^{3+} Lewis acid sites to elucidate how the support influences catalyst structure and catalytic performance in olefin oligomerization. X-ray absorption spectroscopy (XAS) analysis reveals that Ga^{3+} ions with four Ga-O bonds at 1.84 Å interact differently with SiO_2 and Al_2O_3 supports, with two Ga-O-Si bonds at 3.12 Å and four Ga-O-Al bonds at 3.23 Å. Pyridine infrared spectroscopy confirms the presence of Lewis acid sites without Brønsted acidity on both catalysts, with Ga/SiO_2 exhibiting stronger Lewis acidity. Despite similar oligomerization rates, the catalysts exhibit distinct product distributions. At elevated temperatures used for heterogenous catalysts, however, non-oligomer products are formed, including alkanes, non-terminal and branched olefins, and odd-carbon-numbered olefins, for example, from ethylene. While the formation of alkanes and non-terminal olefins is consistent with metal-hydride and metal-alkyl intermediates, the presence of branched and odd-carbon-numbered olefins suggests additional elementary reactions that are not yet understood. To understand the reaction pathways for non-oligomers, a series of reactions with heterogenous Ga^{3+} Lewis acid catalysts is investigated using a combination of experiments and density functional theory (DFT), and microkinetic modeling. Double-bond isomerization was confirmed through 1-hexene reactions, forming internal olefins, while methyl isomerization occurs with low selectivity. Under conditions with low olefin concentrations generated from hexane dehydrogenation, hydrocracking becomes the dominant pathway, producing C_1-C_5 hydrocarbons. DFT calculations

confirm that both double-bond isomerization and β-carbon bond cleavage are energetically feasible and proceed via Ga-hydride and Ga-alkyl intermediates. Microkinetic analysis further supports a mechanism involving hydride transfer and carbanion-like intermediates, distinct from the carbenium ion chemistry of Brønsted acid catalysts. These findings establish mechanistic insights into hydrocarbon reactions on Lewis acid sites and identify previously unreported reactions, including methyl isomerization and olefin cracking.

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