Thermally and Electrochemically Catalytic Ethane Dehydrogenation

Jian Pan
Advisor: Prof. Raul F. Lobo
Committee Members: Prof. Bingjun Xu, Prof. Feng Jiao, Prof. Marat Orazov

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Ethylene is an indispensable part of the modern chemical industry, and its production has been a popular topic in both academia and industry. Given the abundant reserves of shale gas, cheaper ethane in it is likely to replace the expensive naphtha as the feedstock. To realize ethylene production in green and efficient ways with less energy consumption and greenhouse gas emissions, ethane dehydrogenation is a promising alternative to the traditional steam cracking process. The central theme of this dissertation is to explore the possibilities of ethane dehydrogenation for energy-efficient ethylene production.

The major challenges for ethane dehydrogenation at present include the development of novel active and stable catalysts, the establishment of a deep understanding of the catalysts and the catalytic processes, as well as the break of thermodynamic limitations in non-oxidative ethane dehydrogenation. This dissertation presents novel metal-zeolites-based catalysts with excellent activities and employs various advanced techniques to characterize the catalysts and understand the catalytic process. Besides, a solid state electrolyzer has been built and utilized to push the reaction beyond the thermodynamic limitations.

In the first part, Ga- and In-exchanged chabazite (CHA) zeolites with the same Si/Al and metal/Al ratios were prepared via the incipient wetness impregnation method, were characterized using N_2 adsorption, electron microscopy, temperature-programed reactions and were evaluated for the ethane dehydrogenation reaction using flow microreactors. Ga-CHA has higher reaction rates and a lower activation energy of 107 kJ/mol than In-CHA (E_a = 175 kJ/mol). Rietveld refinement of the X-ray powder diffraction pattern shows that the In^+ cation is predominantly located above the 6-ring of the CHA cage. It is proposed that the reaction proceeds through the alkyl mechanism based on the stability of alkyl hydride intermediates as determined using DFT calculations. The oxidative addition of ethane to the metal shows much lower Gibbs free energy for Ga-CHA (+27.95 kJ/mol) vs. In-CHA (+124.85 kJ/mol). These results indicate that oxidative addition may be the rate-limiting step of ethane dehydrogenation in these materials.

The second part presented a new class of Mn-containing zeolites prepared by incipient wetness impregnation (IWI) which can catalyze the ethane dehydrogenation reaction with high selectivity (98%+). Preparation by IWI leads to the formation of Mn_2O_3 nanoparticles on the external surface of the zeolite crystals and herein is shown that the primary active sites for the reaction are located on the surface of these particles. Propane dehydrogenation is also successfully catalyzed by this catalyst. Other Mn-zeolites (MFI and BEA) also have high reactivity and selectivity towards light alkane dehydrogenation.

In addition, it has been shown that the Mn-ZSM5 catalyst has high reaction rates, C_2H_4 selectivity, and stability for ethane dehydrogenation reaction. The specific reaction rate increases with the loading of Mn until the optimal Mn loading amount of 4.6 wt.% for zeolites with a Si/Al

ratio of 12. Structure characterizations and spectra analysis have unveiled that this catalyst contains MnO_2 nanoparticles on the zeolite external surface and $(MnOH)^+$ groups on the external surface of the zeolite. The MnO_2 nanoparticles contain the catalytic sites for ethane dehydrogenation while the $(MnOH)^+$ groups help stabilize the oxides, leading to the high stability of the Mn-ZSM5 catalyst for EDH. As a result, the Mn-ZSM5 samples can catalyze EDH for over 150 hrs at 600 °C with a high reaction rate (>10 $mmol_{C2H6}/g_{cat}/hr$) and high C_2H_4 selectivity ($>98\%$). The spent catalyst can also be regenerated by calcination in dry or wet air (3% steam).

Furthermore, to explore the potential of breaking the thermodynamic limitations, the last part investigated electrochemical ethane dehydrogenation. A solid state electrolyzer was built and employed to realize the removal of H_2 produced during ethane dehydrogenation at the anode side which can be regenerated at the cathode side. This successfully helped increase ethane conversion by 22%. Multiple characterizations have been utilized to understand the reaction process and the migration of oxygen ions was observed which participated in the reaction as well.