Kinetic Modeling of Light Paraffin Aromatization on ZSM-5 based Catalysts

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A detailed kinetic model for light paraffin aromatization has been developed on the basis of the following types of reactions: adsorption/desorption, oligomerization/β-scission, hydride transfer, alkylation, aromatization, unimolecular protolytic cracking and dehydrogenation (Figure 1). The Haag-Dessau mechanism involving the protonation of an alkane to give carbonium ion transition states that collapse to give alkanes (or dihydrogen) and adsorbed "carbenium ions" is considered as the mechanism for alkane activation. Since it is now established that the adsorbed species formed in hydrocarbon reactions over HZSM-5 are surface alkoxy species (1-3) the proposed model assumes that the reactions of these neutral surface alkoxy species take place through carbenium ion transition states; thereby explaining why selectivity patterns are controlled by the ordering of activation energies rather than the relative stabilities of tertiary, secondary, and primary alkoxy species.

The proposed scheme generates 302 reactions. To reduce the number of parameters involved, the reactions have been categorized into various groups, and all reactions in a particular group have been assumed to have the same rate constant. The resultant reaction network consists of 34 reaction families, each of which is parameterized in terms of either a rate constant or an equilibrium constant. Transition state theory bounds the pre-exponential factors and literature values bound the activation energies and provide interrelationships (4-6) between various reaction families. Carbon number dependence within reaction families is incorporated in terms of a linear relationship between activation energy and carbon number. A supplemental model for Ga/ZSM-5 with the active site being a Lewis acid-base pair comprised of a GaH_2 species and a basic framework oxygen (7) is also developed. The added metal function provides additional hydrogenation/dehydrogenation and hydrogenolysis pathways resulting in an additional 72 reactions and 8 reaction families. Translation of the chemistry rules to a set of differential and algebraic equations describing the reactor performance and a robust genetic algorithm search for optimal parameters were achieved by using the reaction modeling suite, a set of computer tools specifically designed for the purpose.

A complete forward predictive model for catalyst design (8) requires the development of a *catalyst chemistry model* that connects chemical and structural descriptors of the catalyst (e.g., Si/Al ratio, charge and size of the transition state, metal loading, etc.) to the kinetic and equilibrium constants of the kinetic model. In this context, we give special attention to the interrelationships and constraints between the various kinetic and thermodynamic parameters that this model archives,

thus connecting fundamental descriptors of the material to its chemistry and hence, performance. These studies of the fundamental relationships between catalyst chemistry and reaction rates include computational studies (at the B3LYP/6-31g(d) level of DFT theory) of olefin adsorption and cyclization employing a cluster model of HZSM-5. Accordingly, elucidation of the essential reaction pathways and kinetics that describe the catalytic behavior of this system will be discussed and the procedure set in the context of a generic framework for catalyst design and development.

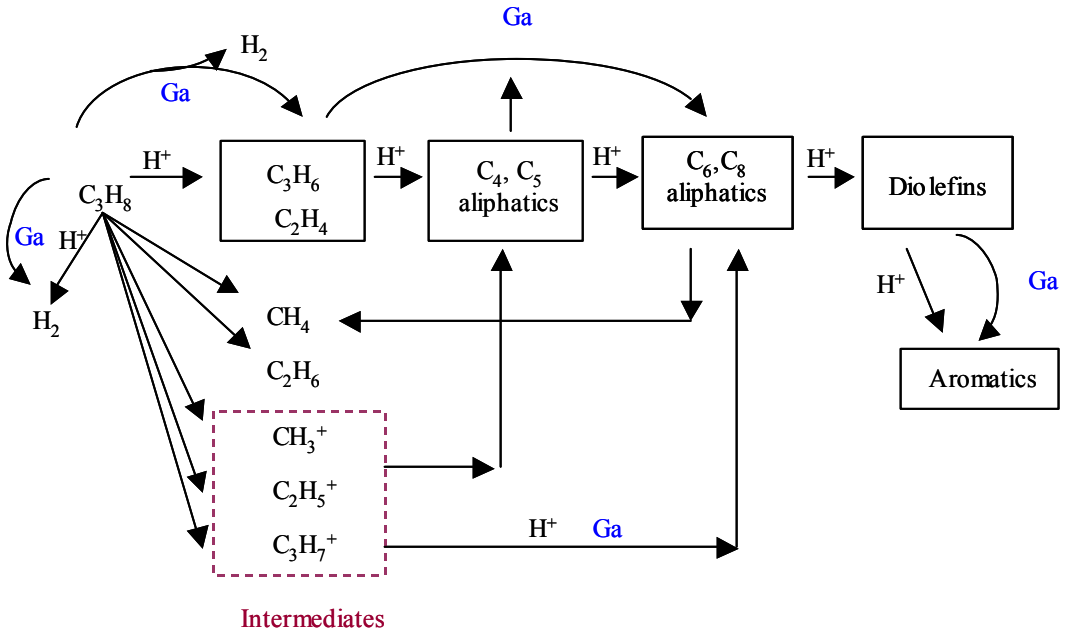

Figure 1. Overall Mechanism for Paraffin Aromatization on Ga/ZSM-5 catalysts

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