4r An Integrated Approach to Catalytic Systems

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My outlook towards materials and catalytic chemistry is focused on answering the question, given a target performance, what is the optimal material composition or formulation to meet those design objectives? In heterogeneous catalysis several approaches have been formulated to answer this question. Recent advances in synthetic methodologies used to control nanometer-sized assembly, high-throughput experimentation as well as the ability to computationally probe catalytic activity are offering unprecedented opportunities to optimize catalyst formulation and activity. I view these approaches not as independent concepts, but as constituents of a broader materials design paradigm. My long term approach is to explore an integrated approach comprising novel material synthesis techniques, combinatorial experimentation, quantitative modeling techniques and *ab initio* computational methods for the discovery and development of catalytic materials [1]. My proposed research will initially focus on developing a repertoire of inorganic and organic-inorganic hybrid, nanometer-sized, synthetic building units based on zeolites, postsynthetic derivatized periodic mesoporous silica materials and clay structures in an effort to design catalytic materials that accurately and efficiently control hydrocarbon-based reaction pathways. This work will be strongly supported by DFT computational studies as well as microkinetic modeling efforts in an attempt to develop an integrated approach to catalytic systems.

Specifically, my Ph.D. research has focused on the conversion of light alkanes to aromatics over ZSM-5 based materials in the following areas:

Microkinetic Modeling for Propane Aromatization: Reaction kinetic studies of propane conversion to aromatics were conducted on an HZSM-5 zeolite at a pressure of 1 atmosphere, temperatures in the range 793-823 K and different space times (5-30 gm-cat hr/mol). The rates of production of methane, ethane, ethene, propene, propane, butane, butene, benzene, toluene and xylene have been measured and a kinetic model has been postulated that considers surface species to be neutral alkoxides, reactions of these alkoxide species by carbenium-ion-like transition states and alkane activation by carbonium-ion-like transition states. The associated elementary steps, categorized within the following reaction types: adsorption, desorption, unimolecular protolytic cracking and dehydrogenation, beta-scission, oligomerization, hydride transfer, alkylation, dealkylation and cyclization, were parsed into reaction families based on an equal reactivity assumption. The 311 reaction steps were grouped in 37 reaction families and the number of unknown parameters was reduced to 25 by using adsorption parameters for n-alkanes and relative rates for beta-scission and hydride transfer from the literature. This kinetic model gives a good fit to the reaction behavior over the HZSM-5 catalyst and details rate constants and activation energies for each of the elementary steps involved in the aromatization chemistry over HZSM-5 catalysts [2]. A supplemental model describing the additional hydrogenation/dehydrogenation and hydrogenolysis functions due to the addition of extraframework gallium has also been developed.

DFT Studies of Olefin Adsorption and Cyclization: We have employed the cluster approach to investigate the protonation mechanisms of olefins in HZSM-5 at the DFT level of theory and have evaluated the influence of cluster size, olefin carbon number, olefin conformation, aluminum siting, and bonding configuration of the alkoxide intermediate [3]. We show the transition states to be carbocationic in nature and evaluate the activation energy to scale with the protonation site (primary, secondary or tertiary) on the olefin. Steric effects and interaction of the protonated molecule with the zeolite wall were observed to play a major role in the stability of the alkoxide species formed. The calculations provide interrelationships between the various kinetic parameters for the model described. We have also employed DFT to elucidate the elementary steps and competing pathways in cyclization of the gas phase carbenium ion species [4]. Current efforts are focused on understanding cyclization of the covalent alkoxide species in the zeolite cavity.

High-Throughput Experimentation and Parameter Estimation: My research also involved the development and operation of an 8-channel high-throughput catalytic reactor system equipped with parallel GC and GC/MS capabilities. The above reactor system incorporates the traditional plug flow arrangement, employs orifices to balance flow, enables temperature measurement in each channel and is capable of giving quantitative product analysis for a complex hydrocarbon mixture for 8 reactors in a time of two hours. An additional focus of my research has been the development of parameter estimation tools for complex kinetic systems such as the one described above [5].

Postdoctoral Research: My postdoctoral research is part of the Methane Conversion Cooperative (MC^2) alliance between British Petroleum (BP) and the University of California at Berkeley. The focus of this long-term alliance is to explore challenging new possibilities in methane chemistry. Specifically, my research will focus on the halide-free catalytic carbonylation of dimethyl ether (DME) over zeolite based materials.

Previous research in our group has demonstrated highly selective conversion of DME to methyl acetate over an H-MOR catalyst. Parallel to on-going research exploring the kinetic behavior of this system, my research will focus on spectroscopic, isotopic and theoretical studies that aim to elucidate the mechanism of this reaction. Current research is focusing on IR studies of low temperature CO adsorption to characterize the acidity of these zeolite materials, DFT studies to understand the nature of binding of CO and DME on these materials and isotopic studies to determine the reversibility of the C-O bond cleavage in DME as well as the details of CO insertion for this reaction.

[1] "Catalyst Design: Knowledge Extraction from High-Throughput Experimentation", *Journal of Catalysis*, **216** (2003) 98.

[2] "Microkinetic Modeling of Propane Aromatization on HZSM-5", *Journal of Catalysis* (in review) (2005).

[3] "DFT Investigation of Alkoxide Formation from Olefins in H-ZSM-5", *J. Phys. Chem. B* **107** (2003) 10476.

[4] " A DFT-Based Reaction Pathway Analysis of Hexadiene Cyclization via Carbenium Ion Intermediates: Mechanistic Study of Light Alkane Aromatization Catalysis", *J. Phys. Chem. B* **108** (2004) 971.

[5] " A Hybrid Genetic Algorithm for Efficient Parameter Estimation of Large Scale Reaction Networks", *Computers and Chemical Engineering* **28** (2004) 2569.