Propane Aromatization on ZSM-5-based Catalysts: A Modeling Perspective

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Introduction

This work focuses on the design of catalytic materials for the conversion of the light alkane propane to the value-added products aromatics and hydrogen on ZSM-5-based catalysts and uses the Discovery Informatics methodology, a model-based approach of extracting knowledge from data. The development of a robust microkinetic model for this system, involving the study of catalytic descriptors such as Si/Al ratio, percent metal content and catalyst structure, constitutes the primary goal of the work. In particular, we are studying the effects of gallium addition to HZSM-5, a method known to enhance the dehydrogenation ability of the catalyst as well as effects of variation of the Si/Al ratio. Experimental results suggest an optimum in propane conversion and aromatics selectivity with gallium loading and significant effects of the Si/Al ratio. Models which capture this behavior are structured to aid in the selection of catalyst composition to optimize desired products.

Materials and Methods

HZSM-5 catalysts were tested for crystallinity by X-Ray Diffraction (XRD) while particle size was established by Transmission Electron Microscopy (TEM). Atomic absorption spectroscopy revealed elemental compositions while FTIR and ^{27}Al MAS NMR experiments established the coordination of Al species. Ga/HZSM-5 catalysts were synthesized by the incipient wetness impregnation technique and pre-treated in hydrogen at 530°C before reaction measurements.

Propane aromatization was performed on these HZSM-5 and Ga/HZSM-5 materials at 1 atm pressure, temperatures ranging from 510°C to 550°C, space times varying from 2 to 8 g_{cat} hr/mol and a wide range of Ga/Al and Si/Al ratios. The main constituents of the outlet gas stream, methane, ethane, ethylene, propylene, butane, butene, benzene, toluene and xylene, were quantified using a Gas Chromatograph (GC) equipped with a capillary column connected to a Flame Ionization Detector (FID).

Results and Discussion

A quantitative model using 312 elementary steps and 25 rate and equilibrium parameters to describe the aromatization of propane over HZSM-5 with Si/Al of 16 (supplied by ExxonMobil) [1] served as the base case against which to compare new results. Ga/HZSM-5 catalysts showed a steady decline in the strength of the 3610 cm^{-1} band with Ga content when characterized by FTIR spectroscopy at room temperature, suggesting a fall in brønsted acidity with gallium addition. We also observed propane conversion and aromatics selectivity to maximize at a Ga/Al ratio of about 0.5 (Figure 1). Our experimental observations thus point to a synergistic interaction between the proton and gallium sites. Kinetic models based on three different Ga active sites, including GaH^{2+} [2], GaH_2^+ and gallium that does not annihilate proton sites, were first used individually to describe the full dataset. We will present an evaluation of these models based on an assigned catalytic functionality for these sites and the associated parameters. The final model combines these functionalities in a unified description of the catalytic behavior to give the best fit to the data.

Kinetic experiments on HZSM-5 with varying Si/Al ratios (supplied by U.O.P.) confirm the expectation that propane conversion has a linear dependence on the aluminum content. They also show a constant conversion decrease in fuel gas production and linear increase in the benzene/toluene ratio with Si/Al, suggesting the dependence of cracking and alkylation-dealkylation reactions on Si/Al. The implications of this behavior on the proton kinetic model and its rate parameters will be discussed.

Significance

The activation of light alkanes and their selective conversion to the value-added products, aromatics and hydrogen has both fundamental and practical impact. Aromatics (BTX) are a valuable source of the world's petrochemicals and find applications in a wide range of products. From a modeling point of view, the complexity of the chemistry and thereby the large dimensionality of kinetic models involved requires development of effective tools to handle the size of the problem while still accounting for the effects of experimental error. Incorporation of complex microkinetic models into a rational catalyst design strategy also broadens the application of model-based design approaches to the discovery of catalysts for specialty chemicals applications.

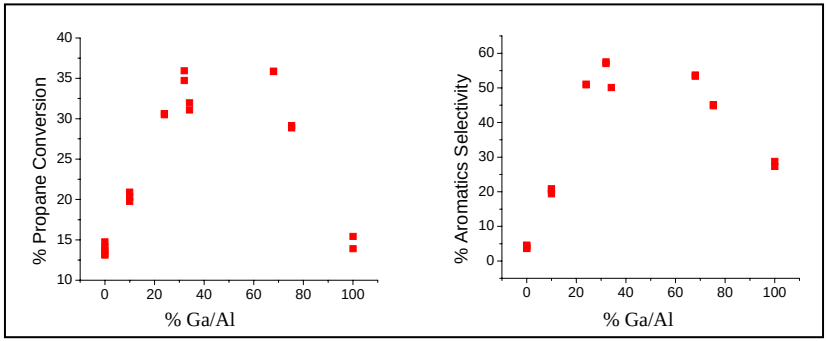

Figure 1. Gallium Optimum Data (Si/Al = 16, T=520°C, tau=1.5g-hr/mol)

References

1. Bhan, A., Hsu, S.H., Blau, G.E., Caruthers, J.M., Venkatasubramanian, V., and Delgass, W.N. *Journal of Catalysis* 235(1), 35 (2005).
2. Joshi, Y.V., and Thomson, K.T. *Catalysis Today* 105, 106 (2005).