

Fundamental Insights into Hydrocarbon Conversion Mechanisms in Lewis and Brønsted Acid Zeolites using Temporal Analysis of Products

Hari Thirumalai, Jeffrey D. Rimer and Lars C. Grabow*
Department of Chemical and Biomolecular Engineering, University of Houston,
Houston, TX 77204-4004 (USA)
*grabow@uh.edu

Introduction

The surge in natural gas production has hastened the search for processes that can utilize methane and light olefin derivatives in the manufacture of useful products such as benzene, toluene and xylene (BTX). Industrial demand is met through processes such as the synthesis of BTX through dehydroaromatization of light olefins or through alkylation of aromatics, typically with the use of zeolites as catalysts. Reaction mechanisms determined by the presence of a hydrocarbon pool (HP) dominate the chemistry and are challenging to study.^{1,2} In this work, we use the transient kinetics technique, temporal analysis of products (TAP), to probe hydrocarbon conversion and upgrade in the transient regime of reaction. TAP experiments help probe the intrinsic kinetics of reactant conversion in a well-defined Knudsen transport regime under high-vacuum conditions. We studied the dehydroaromatization of ethylene and the methylation of toluene as case-studies for hydrocarbon conversion reactions.³

Materials and Methods

Ag-ZSM-5 catalysts were synthesized by ion-exchange with AgNO₃ and subsequently calcined and characterized by XPS, XRD, UV-vis and XAS techniques.³ TAP transient kinetics experiments were performed on the TAP-1 reactor, under typical conditions of high vacuum with relevant reactant streams depending on the type of reaction under study.⁴ A schematic of the TAP technique is given in Figure 1. The pulse responses were monitored at the reactor exit by an UTI 100C online mass spectrometer (MS). Appropriate calibration experiments were performed to convert the MS signal into molar quantities and final processing was done to remove contributions from overlapping hydrocarbon fragments.

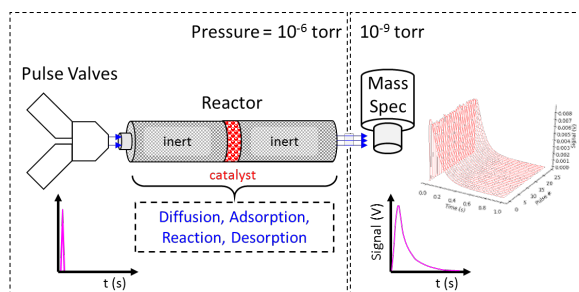


Figure 1: Schematic of the temporal analysis of products technique

Results and Discussion

The precise control and quantification of species participating in the transient chemistry suggest that a Lewis acid such as Ag⁺ or Ga³⁺ in the zeolite accelerate the retention of long lived carbonaceous species in the zeolite, thus attaining the autocatalytic arene cycle more rapidly. This is evidenced by the C₂H₄ pulse and the C₄H₈ product responses shown in Figures 2a) and 2b), respectively. The long tail of the C₂H₄ pulse response over H-ZSM-5 and the complete absence of C₄H₈ signal over Ag-ZSM-5 samples provide

qualitative evidence that olefins are strongly bound to the metal-exchanged zeolite samples due to delayed desorption. The Lewis acid also increases the rate of production of H_2 and C_6H_6 (Figure 2c), indicative of an enhanced rates of dehydroaromatization.

Finally, experiments investigating the methylation of toluene to xylene provide valuable information on competitive binding of reactants to the zeolite acid sites and the ensuing primary reactions that drive the reaction. The number of moles of toluene entering the reactor appears to have a pronounced effect on the kinetics of xylene formation, suggesting a complex relationship between the dual-cycle HP mechanism and the desired toluene methylation reaction.

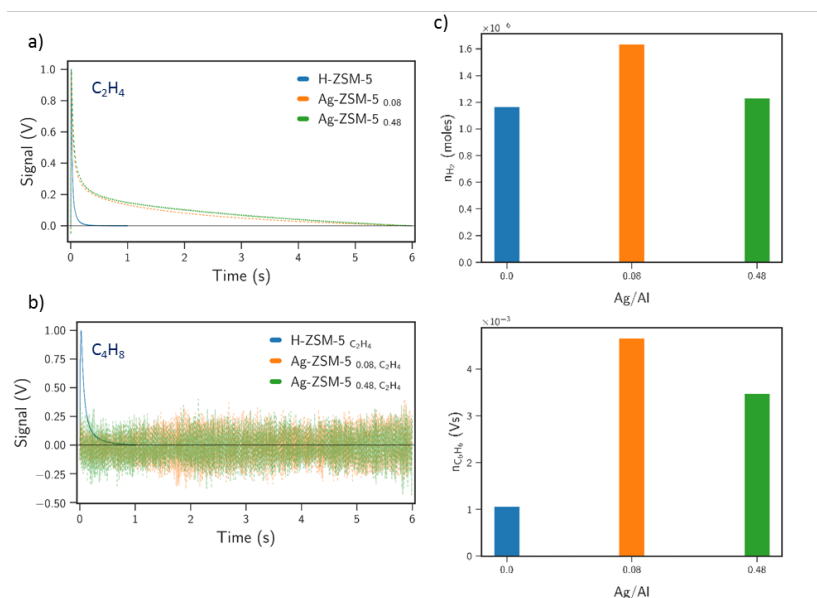


Figure 2: Averaged pulse responses for a) C_2H_4 and b) C_4H_8 produced for different samples studied for C_2H_4/He single pulse experiments at $400^\circ C$. c) Total moles of H_2 and C_6H_6 formed for the same samples.

Conclusions

We have investigated the transient initiation period of typical hydrocarbon upgrade reactions that utilize zeolites as catalysts. The primary alkene dimerization and toluene alkylation reactions occur at Brønsted acid sites. Lewis acid sites (Ag^+ , Ga^{3+}), interact strongly with olefins and increase the selectivity towards aromatic products and accelerate the aromatic producing arene cycle of the HP mechanism. These insights enable the realistic exploration of potential energy surface through *ab initio* simulations, thus providing a mechanistic understanding of the chemistry. This understanding provides a framework for the design of tailored catalysts for cascading reaction schemes over multiple, functionally distinct, reaction sites.

References

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