

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

In the first year of this award, we used the transient kinetics technique, temporal analysis of products (TAP), to probe the dehydroaromatization of ethylene and the methylation of toluene as case-studies for hydrocarbon conversion reactions in the transient regime of reaction. The precise control of reactant molecules entering the reactor and responses recorded by a high-resolution mass spectrometer at the reactor outlet in the dehydroaromatization of ethylene suggest that a Lewis acid such as Ag^+ in the zeolite accelerate the retention of long lived carbonaceous species in the zeolite, thus accelerating the attainment of the autocatalytic arene cycle. During the first year of our project, we were able to obtain preliminary TAP data. For example, pulse responses in Figure 1a provide qualitative evidence that olefins are strongly bound to the metal-exchanged zeolite samples with delayed desorption compared to paraffins of the same carbon number, thus enhancing the rate of hydrocarbon conversion and carbon retention. Mean residence times of C_2H_4 pulses exiting H- and Ag-ZSM-5 ($\text{Ag}/\text{Al} = 0.08$) catalysts in Figure 1b and density functional theory (DFT) computed binding energies of various olefinic species in Figure 1c confirm the stabilizing role of extra-framework Ag^+ cations in ZSM-5.

The acid-catalyzed methylation of toluene with CH_3OH over H-ZSM-5 was also studied by means of carefully controlled pump-probe experiments. In these experiments, pulses of CH_3OH (pump) were followed by pulses of toluene (probe) at a pre-determined time delay (Figure 2a) and the transient evolution in products formed was monitored. Figure 2b-d depicts the effect of delay time on the formation of xylene and H_2O , the primary products of toluene methylation. Preliminary results indicate that the interaction of a toluene pulse with unreacted methanol in the zeolite or highly active methanol intermediates increases the yield of xylene produced at lower toluene conversions. Increasing the separation in time between CH_3OH and toluene pulses allows for the CH_3OH to undergo reactions that consume active species necessary for the methylation of the subsequent toluene pulse. These results also suggest that higher reactant partial pressures increase the selectivity of the chemistry towards the formation of desired xylene.

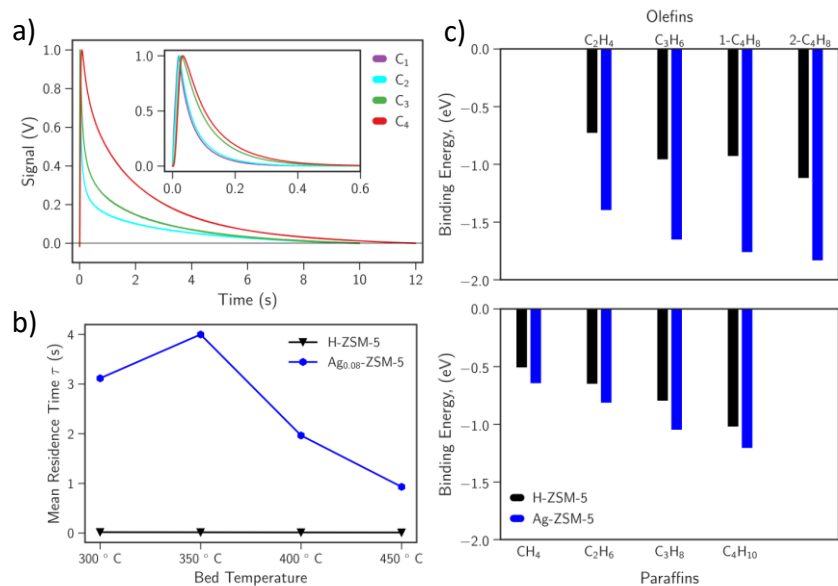


Figure 1: a) Averaged pulse responses of olefins and paraffins (inset) over Ag_{0.08}-ZSM-5 (where 8% of Al sites are exchanged with Ag⁺). b) Mean residence times of average pulses of C₂H₄ over Ag_{0.08}-ZSM-5 as a function of temperature. c) Binding energies of olefins and paraffins over H-ZSM-5 (black) and Ag-ZSM-5 (blue) calculated by DFT using periodic cell models.

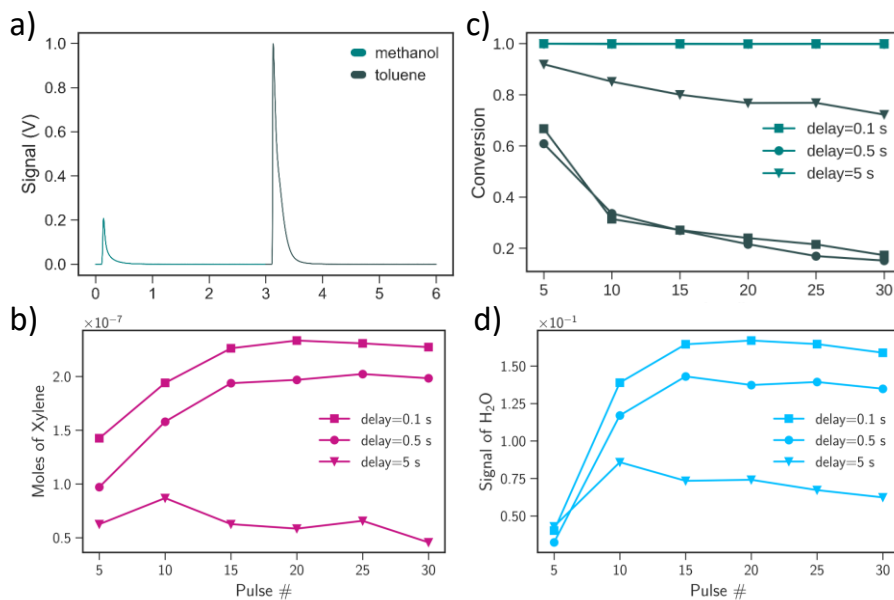


Figure 2: a) Depiction of methanol and toluene pulses in the pump-probe experiments performed on the TAP reactor. b) Toluene and methanol conversions over the course of the experiment, with corresponding c) yields of xylene and d) total signal for H₂O obtained as a function of pulse number.