

1. PRF# 57390-ND5**2. Project Title:** ZrO₂-Based Alternatives to Precious Metal Catalysts for Naphtha Reforming: Kinetics, Mechanism, and Site Requirements for (cyclo)Alkane Dehydroaromatization**3. P.I. Name, Affiliation:** Aditya Bhan, University of Minnesota**4. Co-PI (if any), Affiliation:** N/A

Carbide forms of Mo encapsulated in HZSM-5 solid acids catalyze CH₄ dehydroaromatization (DHA) at yields close to those prescribed by equilibrium. Exposure to CH₄ at high temperatures (≥ 950 K) reduces and carburizes oxidic Mo precursors to form molecular-size MoC_x clusters which activate C-H bonds in methane to initiate C-C coupling reactions that lead to aromatics. Mo/H-ZSM-5 catalysts convert methane to benzene ($6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2$) at $\approx 70\%$ selectivity, but are incapable of surpassing thermodynamic limits on single-pass conversion ($\sim 10\%$ at 973 K) set by reaction endothermicity[1-3]. Our efforts in circumventing this challenge center on introduction of an additional metal function that transiently absorbs hydrogen and thereby overcomes the intrinsic thermodynamic limitations in methane upgrading.[4] Proximity effects during absorptive hydrogen removal can be rigorously described by hydrodynamic bed-scale packed-bed reactor models that consider characteristic diffusive and convective rates controlling mobility of gas-phase H₂ which effectively couples catalytic-absorptive sequences at sites distinct in function and spatial location.

Topic 1: Introduction of Zr successfully couples C-H activation and H₂ removal lifting equilibrium constraints on single-pass methane conversion and enhancing aromatic yields by $\geq 2x$ in all fixed-bed configurations (Figure 1a). The absorptive function results in formation of bulk ZrH_x species as affirmed in X-ray diffraction and thermal desorption studies, and can be regenerated by isothermal treatment in He flow at 973 K. The observed enhancement in DHA yields for staged-bed reactor configurations can be described based on a model that considers back-mixing of hydrogen at the bed-scale to result in a dispersed flow packed-bed reactor. A reaction-transport model that incorporates kinetic, diffusive, and convective length and time scales based on dimensionless parameters Damköhler number, $Da = kL/u$, and Péclet number, $Pe = uL/D$, which depend on catalyst bed-length, L, linear flow velocity, u, rate constants, k, and effective diffusion coefficients, D, quantitatively describes the effects of proximity between the catalytic and absorptive functions (Figure 1b).

Topic 2: Mo-modified H-ZSM-5 catalyzes methane dehydroaromatization via a single-path series reaction wherein initial methane activation and C-C coupling to ethane is followed by sequential dehydrogenation to ethylene and acetylene, the immediate stable gas-phase intermediate to benzene formation. Elucidation of the dehydroaromatization reaction network and quantification of reversibility of intervening dehydrogenation and oligomerization reactions is achieved by change of effective contact time by extent of “non-selective” deactivation. The “non-selective” nature of deactivation is confirmed by congruence of conversion-selectivity curves and permits probe of axial rate and reversibility profiles after determination of $f(\tau)$, the one-to-one function between methane conversion and contact time. Methane, ethane, and ethylene form a quasi-equilibrated pool at contact times beyond $7 \text{ mol}_{\text{Mo}} \text{ s} (\text{mol}_{\text{CH}_4})^{-1}$, resulting in a pseudo-steady state methane aromatization pathway with both rate- and reversibility-determining steps, C₂H₄ dehydrogenation and C₂H₂ dimerization, involving acetylene – identified to be a key reactive intermediate in dehydroaromatization.

Impact of the research

The methane DHA reaction network is elucidated by varying contact time by extent of “non-selective” deactivation to reveal that (i) ethane is the sole primary product of methane pyrolysis and (ii) acetylene is a key intermediate involved in rate-determining and reversibility-determining steps.

The utility of a polyfunctional catalytic-absorptive formulation to accelerate rates of non-oxidative methane conversion to aromatics has been illustrated.

References

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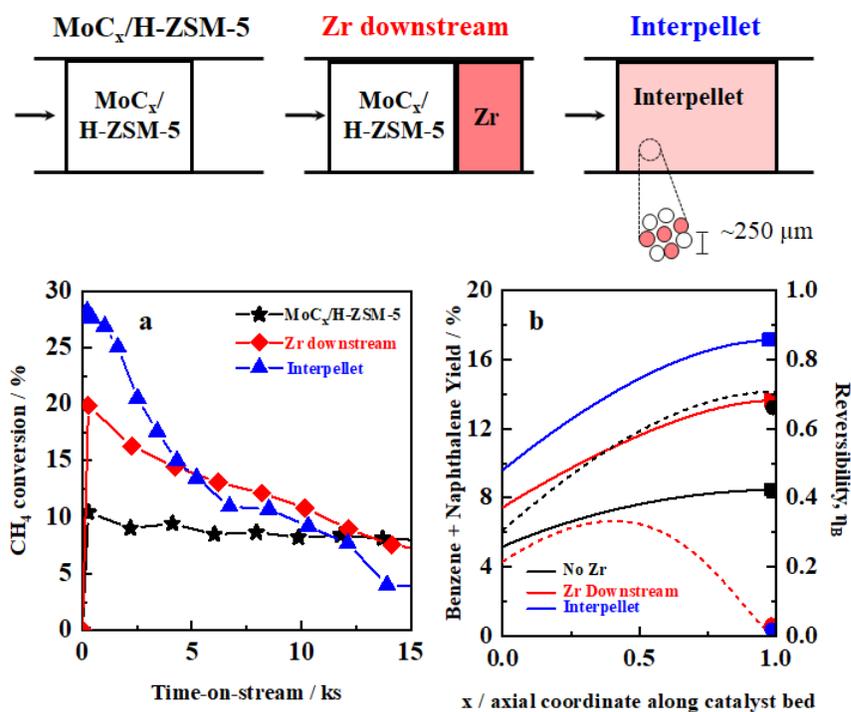


Figure 1. (a) Methane conversion as a function of time-on-stream measured experimentally on Zr + MoC_x/HZSM-5 formulations; observed transients reflect saturation of hydrogen-absorbent. (b) Axial profiles of benzene + naphthalene (B+N) yield (solid lines; left) and reversibility (η_B) for benzene production (dashed lines; right) per simulation of the reaction-transport model. Simulations predict $\eta_B \rightarrow 0$ throughout the bed for interpellet mixtures. Solid squares and circles are experimentally observed effluent B+N yield and η_B , respectively.