Microwave-Driven Intensification over Cerium-Zirconium Oxide Catalysts

Quentin Kim

Advisor: Dionisios G. Vlachos, PhD.

Committee Members: Dongxia Liu, PhD., Raul F. Lobo, PhD., John M. Vohs, PhD.

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The chemical industry accounts for nearly a quarter of U.S. greenhouse gas emissions, with combustion-based process heating accounting for 75% of that contribution. Electrification of reactor heating using renewable electricity is a critical decarbonization pathway, and microwave (MW) heating is particularly promising due to its fast, volumetric, and selective heating behavior. Unlike conventional heating (CH), MWs can interact directly with the catalyst material, enabling non-thermal effects on surface chemistry and reaction kinetics. Cerium zirconium oxide (CZO) is both MW and catalytically active, serving as an interesting model system for this dissertation.

We first establish a mechanistic foundation for CZO reduction dynamics under CH. Transient kinetic experiments and *in situ* spectroscopy reveal that the CZO reduction rate passes through an initial maximum before slowing, consistent with concurrent oxygen removal from the surface and bulk. Complementary molecular simulations indicate that lattice oxygen mobility is maximized at intermediate extents of reduction due to the competing effects of vacancy availability and lattice distortion.

Building on this foundation, we characterize how CZO reduction couples to MW absorption, revealing nonlinear heating dynamics including self-accelerating heating, a critical

reduction threshold, and temperature multistability. Transient and spatially resolved temperature measurements are combined with permittivity characterization. Reactor-scale simulations incorporating these dielectric properties accurately reproduce the experimental heating behavior, providing practical guidelines for MW reactor control.

MW heating is applied to the reverse water-gas shift (RWGS), $CO_2 + H_2 \rightarrow CO + H_2O$, a redox reaction relevant to reforming chemistries. Steady-state, transient, and reactant pulse experiments over CZO and Ni/CZO decouple the oxidizing and reducing half-reactions, revealing that MW irradiation asymmetrically affects the two: H_2O formation is enhanced while CO formation is substantially suppressed. Ni/CZO under MW heating exhibits reduced RWGS activity at elevated temperatures, the first reported instance of MW irradiation inhibiting catalytic activity, demonstrating that MW-catalyst interactions are sensitive to composition and extend beyond simple thermal effects.

Finally, MW heating is applied to the dry reforming of methane (DRM), $CO_2 + CH_4 \rightarrow 2CO + 2H_2$, a promising reaction for industrial decarbonization. MW heating enhances DRM activity three to five-fold over CH at the same temperatures. Direct inter-particle contact between CZO particles is critical to this enhancement. Under CH, Ni/CZO undergoes significant deactivation from coking, requiring temperatures above 800 °C for reactivation after an initial deactivation. MW heating at 700 °C eliminates this deactivation period and yields stable conversions comparable to CH at 800–900 °C without substantially lowering coke formation.