Chemical process electrification: Applications to nitrogen fixation and enhanced catalytic hydrogen production

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Global population growth over the last century has increased fossil fuel consumption, intensifying greenhouse gas (GHG) emissions. Decarbonization of the chemical industry, one of the highest emitting sectors, is key to mitigating GHG emissions and decelerating climate change. Process electrification and intensification present an opportunity for low-carbon, modular and decentralized chemical production. This dissertation explores how non-thermal atmospheric plasmas (NTAP) and resistive (Joule) heating with temperature modulation capabilities can pave the way to new reaction pathways and intensify catalytic processes.

In the first part, we demonstrate single-step, non-thermal plasma-assisted synthesis and identify variables that control selectivity and energy consumption. Chapter 2 demonstrates a catalyst-free, selective, non-thermal plasma assisted hydrogen cyanide (HCN) synthesis method, directly from methane (CH_4) and nitrogen (N_2), bypassing ammonia (NH_3) as the nitrogen carrier. A simplified plasma microkinetic model is developed to elucidate reaction pathways and critical intermediates. The energy consumption and CO_2 equivalent emissions of the electrified process are compared to industrial benchmarks, highlighting the potential for minimal emissions.

In Chapter 3, we present selective nitric acid (HNO_3) production in a biphasic air-water NTAP reactor. High selectivity is linked to reaction of secondary products, nitrous acid and hydrogen peroxide, in the bulk liquid phase. Plasma-liquid interfacial area and treatment time are the most important variables for optimal production rate and energy efficiency.

The second part of the dissertation focuses on dynamic resistive heating for enhancing catalytic activity and accelerating material fabrication. Chapter 4 introduces programmable temperature modulation for enhanced on-demand hydrogen (H_2) production from ammonia over Ru/Al_2O_3. Dynamic operation outperforms steady-state heating and achieves the highest reported H_2 production rate at relatively low average temperature compared to conventional Ru-supported processes. Integrating microkinetic modeling with experimental observations reveals that transient high-temperature exposure promotes surface species desorption, improving catalytic activity.

Chapter 5 extends Joule heating to materials fabrication. We develop an in-situ X-ray diffraction (XRD) Joule-heated reactor to investigate the catalytic nitridation of molybdenum carbide (Mo_2C) during NH_3 cracking under continuous Joule heating (CJH) and rapid pulse heating (RPH). Rapid pulse heating accelerates nitridation and increases energy efficiency, while mitigating catalytic deactivation. Compared to conventional heating, continuous Joule heating promotes bulk nitridation, underscoring its potential for rapid, energy-efficient material synthesis.