

# Dynamic electrification toward sustainable and enhanced catalysis

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## Highlights

- We model the kinetics of dynamic pulsed temperature operation and demonstrate enhanced performance surpassing steady state and thermodynamic limits.
- We demonstrate experimentally enhanced reaction rates for the ammonia decomposition reaction.

## 1. Introduction

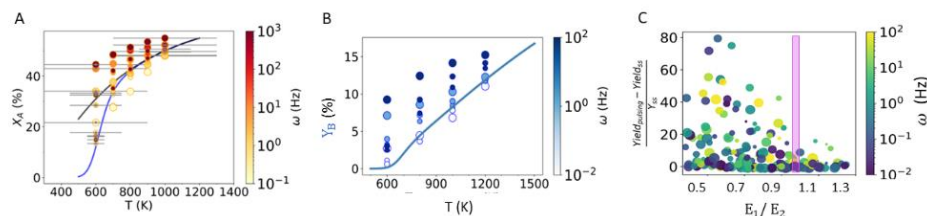
Chemical manufacturing is a major energy consumer and a massive greenhouse gas emitter owing to using natural gas to supply heat and produce key chemicals<sup>1</sup> like ethylene, propylene, and syngas. Electrification using green electricity, particularly Joule heating, offers the potential for decarbonization. Dynamic Joule heating of high-frequency temperature pulses can enhance rate and control selectivity<sup>2-4</sup>. Here, we model the pulse heating's influence on kinetics (1) excluding catalytic effects, using dynamic prototypical models<sup>5</sup> and (2) real complex chemistry and compare to new experimental results for ammonia decomposition.

## 2. Methods

We model prototypical reactions (P1:  $A \leftrightarrow B$  equilibrium limited; P2:  $A \rightarrow B$ ,  $A \rightarrow C$  parallel; P3:  $A \rightarrow B \rightarrow C$  series, linear first order)<sup>5</sup> and the ammonia decomposition on a ruthenium multisite catalyst<sup>6</sup>. We compare time-averaged performance from pulse heating simulations to steady-state results and experimental data. Experiments were conducted on a Ru-based catalyst using our millisecond pulse reactor.

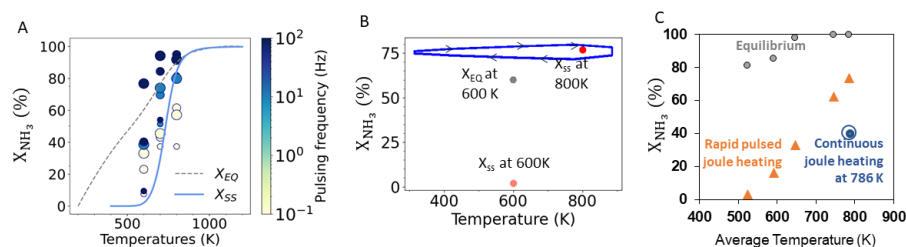
## 3. Results and discussion

*Figure 1* demonstrates key results from the 3 prototypes studied herein. *Figure 1A* displays the conversion (steady state, equilibrium, and pulsing heating) for P1. High-frequency (10-100 Hz) pulsing enhances conversion beyond steady state and equilibrium. *Figure 1B&C* show results for P2 when (B)  $E_1 < E_2$  and (C)  $E_1 > E_2$  where  $E_x$  is the activation energy for reaction  $x$ . Temperature pulsing increases conversion at lower average temperatures with a negligible loss in selectivity, enhancing yield (*Figure 1B*). In Panel C, higher temperature boosts conversion and slightly improves selectivity, resulting in increased yield. For  $E_1 < E_2$  (left of purple line) and low temperatures, higher frequencies significantly improve yield by almost 2 orders of magnitude compared to steady state. It becomes evident that a greater yield enhancement necessitates a separation in time scales, as indicated by the ratio of rate constants (x-axis)<sup>2</sup>.



**Figure 1:** Effect of pulse heating on gas phase endothermic prototypes. (A) P1; (B) and (C) P2. (A) Conversion (colored markers) along with the steady-state and equilibrium conversions (blue and black lines), with the size of horizontal bars corresponding to amplitude of 50, 150, and 300 K. (B) Yields for B where activation energy of  $A \rightarrow B$  is 100 kJ/mol and  $B \rightarrow C$  is 120 kJ/mol; points show pulse heating yields and lines show steady state yields. (C) Yield enhancement vs ratio of activation energies using Latin Hypercube sampling.

This fundamental understanding can be extended to complex chemistries, like ammonia decomposition modelled on Ru steps(S) and terraces(T) with parameters from density functional theory (DFT)<sup>6</sup>. As anticipated from the A $\leftrightarrow$ B prototype model, pulse heating monotonically increases the NH<sub>3</sub> conversion ( $X_{NH_3}$ ), surpassing equilibrium at higher frequencies (>10 Hz) and amplitudes (>100 K) (Figure 2A), consistent with experiments of this work (Figure 2C). The limit cycle in Figure 2B indicates super performance beyond steady state (~50x) and equilibrium (~1.5x) conversion and yields at the same average temperature 600 K using a high frequency pulse. Reaction path analysis and sensitivity analysis reveal (not shown here) an interplay of Ru(S) and (T) sites and interesting catalyst site dynamics. We will discuss catalyst dynamics during the periodic operation of the reactor in detail.



**Figure 2:** Ammonia decomposition at steady state and pulse heating using a full microkinetic model. (A) Conversion vs temperature (blue line: steady state, dashed line: equilibrium; points: pulsing). (B) Limit cycle of conversion at avg. temperature of 600 K, frequency of 100 Hz and amplitude of 300 K. (D) Experimental data of conversion using rapid pulse heating and continuous joule heating (at 786 K) with 10 mg Ru catalyst for 20 ms pulse heating period and 1 Hz frequency duty cycle.

#### 4. Conclusions

We modeled the performance boost observed through dynamic electrification, across various reaction prototype and microkinetic networks. We found that dynamic operation enhances reaction rates and conversion even above equilibrium. We confirmed the modeling results with new experiments for the ammonia decomposition. We provide detailed mechanistic understanding of the reasons for the enhanced performance. Finally, we expose interesting catalyst dynamics and the characteristic time scales.

#### Acknowledgments

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#### Keywords

Electrification; Joule heating; dynamic catalysis; reaction kinetics