

# Unconventional Reactor Performance via Joule Electrification

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## Highlights

- The performance of electrified reactors under dynamic operation can surpass that of conventional steady-state operation.
- We demonstrate that rapid pulse heating (RPH) operation of the CO<sub>2</sub> hydrogenation reaction at 1 bar over a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst increases the reaction rate and shifts the product selectivity toward CO over CH<sub>4</sub> at low reaction temperatures (<500 °C).

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) capture and utilization receive attention due to the greenhouse effect. Its conversion via electrified processes using renewable electricity is environmentally appealing but economically challenging. CO<sub>2</sub> can be reduced to various molecules. At low pressures, CO and CH<sub>4</sub> are the typical products. CO is often preferred over CH<sub>4</sub> as it can easily be transformed into products of greater economic value, such as larger hydrocarbons or oxygenates, via the Fischer-Tropsch synthesis. Ni-based catalysts have been used widely for CO<sub>2</sub> activation due to their low cost and high activity. On Ni-based catalysts, CH<sub>4</sub> formation is almost unavoidable due to the strong adsorption of CO on Ni<sup>0</sup> at low temperatures. Several strategies have been adopted to shift the catalyst selectivity toward CO, including using different supports, tuning the metal particle size, and adding promoters or secondary metal elements.[10,19] These strategies add catalyst development and synthesis cost. Alternative strategies are worth developing to improve selectivity and process efficiency.

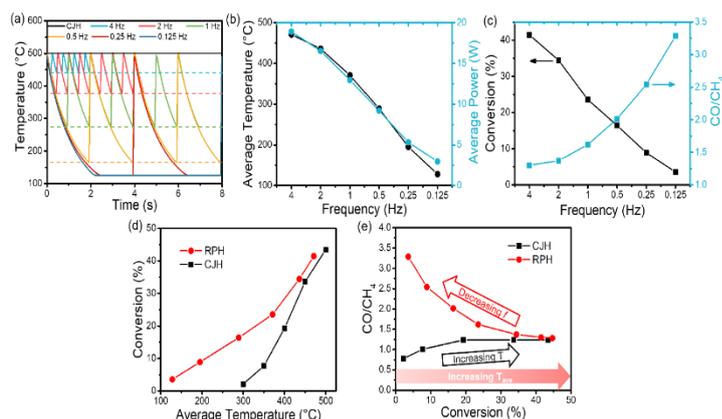
Electrified reactors, utilizing Joule heating, microwaves, or inductive heating, are more compact and versatile than conventional reactors heated by fossil fuel combustion and allow easier manipulation of process parameters, such as temperature, concentration, and pressure, making dynamic operation viable. Dynamic operation far from thermodynamic equilibrium can improve energy efficiency and shift product selectivity.[25–27] However, experimental evidence of selectivity control on heterogeneous catalysts by fast pulsing is generally lacking. In addition, *operando* characterization of catalysts under rapid pulse dynamic conditions at atmospheric pressure has never been conducted before.

This work studies the first reaction network that combines endothermic and exothermic reactions powered by Joule heating. We demonstrate that dynamically operating the CO<sub>2</sub> hydrogenation reaction over a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst tunes the product CO/CH<sub>4</sub> ratio. Extensive *operando* spectroscopic characterization and kinetics reveal the reaction mechanism of CO<sub>2</sub> hydrogenation reaction and suggest a dynamically changing catalyst surface during pulse heating.

## 2. Methods

The Joule heating reactor was described in detail in our previous work.[29] The reactor is a vertical tubular reactor made of quartz (ID = 22 mm), with an opening in the middle to accommodate a ZnSe window for Infrared thermometry. Two stainless steel clamps and four copper plates fix the Joule heating element. A DC power supply provides the current, and a LabView program enables programmable heating. The reactor can be operated in 2 modes: continuous Joule heating (CJH) and rapid pulse heating (RPH). Typically, the circuit is on for milliseconds for the heating element to reach the peak temperature and then off for cooling. The process is repeated to realize fast temperature cycling. The temperature of the carbon fiber paper is monitored by an IR camera (PI640) through the ZnSe window with a frame rate of 125 FPS (frames per second). The voltage and current output of the power supply are recorded, and the power output is estimated.

## 3. Results and discussion



**Figure 1.** CO<sub>2</sub> hydrogenation under continuous Joule heating (CJH) and rapid pulse heating (RPH). (a) Temperature under CJH (black horizontal line at 500 °C) and RPH at various frequencies.  $T_{low}$  of the RPH temperature is indicated with dashed, horizontal lines. (b) Average temperature and estimated average power consumption vs. frequency for RPH. (c) Effect of RPH frequency on conversion and CO/CH<sub>4</sub> ratio. (d) Effect of (average) temperature on CO<sub>2</sub> conversion. (e) CO/CH<sub>4</sub> ratio vs. conversion.

The CO<sub>2</sub> hydrogenation reaction is first conducted in the Joule reactor under continuous heating over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Figure 1d (black line) shows that the CO<sub>2</sub> conversion increases from 2.2% at 300 °C to 43.5% at 500 °C. The product CO:CH<sub>4</sub> ratio (Figure 1e, black squares connected with a line), increases from 0.77 at 300 °C to 1.24 at 400 °C, and then plateaus. The catalyst is stable with time on stream. The equilibrium conversion goes through a minimum with varying temperature due to the co-existence of the two overall exothermic and endothermic reactions; methane is preferred at low temperatures and CO at high temperatures. The CJH reaction data in Figure 1d&e indicates a quite lower conversion than the equilibrium one, i.e., the operation is far from equilibrium.

Next, we investigate the CO<sub>2</sub> hydrogenation under pulsing. The temperature profiles of RPH processes are summarized in Figure 1a. We have programmed the reactor to keep the peak temperature ( $T_{high}$ ) at 500 °C by adjusting the heating voltage while keeping the heating duration fixed at 50 ms. We vary the frequency of pulses ( $f$ ) by adjusting the cooling time. For example, 50 ms heating + 950 ms cooling corresponds to  $f = 1$  Hz, while 50 ms heating + 1950 ms cooling corresponds to  $f = 0.5$  Hz. Due to varying cooling time, the lowest temperature in each cycle ( $T_{low}$ ) changes (indicated by the horizontal lines in Figure 1a). In these experiments,  $f$  varies from 0.125 Hz to 4 Hz. With decreasing  $f$ ,  $T_{ave}$  decreases (Figure 1b), the conversion decreases due to a lower  $T_{ave}$  (Figure 1c), and the power also drops (Figure 1b), due to pulsing less frequently and operating for longer periods of time at lower temperatures with the power off, despite using a higher pulsing voltage. During the excursion to higher temperatures, the catalyst is activated, and the time average conversion, while low, is significantly higher than under continuous heating at a similar  $T_{ave}$  (Figure 1d). Rate enhancement has also been reported for other reactions. The CO/CH<sub>4</sub> ratio is a strong function of frequency (Figure 1c, cyan line). As  $f$  decreases and the average temperature drops, the CO/CH<sub>4</sub> ratio increases, i.e., dynamic operation favors CO over methane. The change in selectivity is profound for our conditions; the ratio increases from ~0.75 to ~3.3. What is unexpected is that CO is dynamically favored at low average temperatures where thermodynamics favors CH<sub>4</sub>. This is another manifestation of far-from-equilibrium operation. RPH and CJH at similar conversions give different selectivity (Figure 1e).

#### 4. Conclusions

We demonstrated that rapid pulse heating of CO<sub>2</sub> hydrogenation reaction accesses a product distribution (high CO selectivity) that cannot be reached by conventional steady-state operation under similar average reaction temperatures or conversions. Steady-state *operando* FTIR suggests that \*CO is a key surface reaction intermediate, while transient FTIR spectroscopy and kinetic studies reveal that the reaction mainly proceeds through a sequential redox pathway on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst under these conditions. Pulse heating *operando* FTIR reveals a dynamic catalyst surface with transient coverages of reaction intermediates, where \*CO species desorbs more readily in the presence of \*H. We propose that pulse heating facilitates the formation of these species. This work emphasizes the effect of pulse heating on the coverages of surface species on a catalyst, which alters the reaction pathways. We believe that the concept of shifting the product selectivity by dynamic operation may be extended to other reaction systems where multiple reactions and products compete.

#### Keywords

Pulse heating, dynamics, electrification, Joule heating, spectroscopy, CO<sub>2</sub> hydrogenation.