

Reaction engineering in plasma catalysis: Effect of process parameters on plasma catalytic CO₂ hydrogenation

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Highlights

- Systematic investigation of process parameters of plasma catalytic CO₂ hydrogenation.
- Effect of Ar addition to the NTP catalytic system was revealed.
- Residence time affected the system performance significantly.
- Frequency of the power source plays a key role in improving the performance.

1. Introduction

Compared to the conventional thermal catalysis, electrified processes can be more effective and efficient to enable the CO₂ activation and conversion. Exemplified by nonthermal plasma (NTP) catalysis, it can enable various challenging reactions such as CO₂ conversions and ammonia synthesis under near ambient condition [1-4]. Although significant developments in the fields were made over the last decade, the reaction engineering aspect of the hybrid systems was overlooked. Accordingly, using CO₂ hydrogenation as the model system, we investigated the effect of various process parameters (such as residence time and frequency) on the performance systematically.

2. Methods

The NTP-catalytic CO₂ hydrogenation was conducted using a dielectric barrier discharge (DBD) plasma reactor (with a quartz tube of 8 mm o.d. × 6 mm i.d.) with a tungsten needle as the high-voltage electrode in the center of the reactor and a copper mesh (wrapping around the reactor) as the grounding electrode. Input voltage was monitored using an oscilloscope (Tektronix, TBS1000C) and a high-voltage probe (Tektronix, P6015A), and the plasma discharge was ignited using a power supply. The Ni catalyst (~320 mg, 450–600 μm) was packed in the discharge zone and held by quartz wool and reduced in situ Prior to the catalysis. To initiate the NTP-catalysis, a gas mixture of H₂/CO₂ was introduced into the DBD plasma reactor by mass flow controllers. The applied peak voltage, current and frequency were varied to study their effects on the performance of the system. Residence time and Ar addition were investigated as well. The dry gas composition from the outlet of the reactor was analyzed using a gas chromatograph (GC9720Plus). In-situ optical emission spectroscopy (OES) was conducted to probe the species in the discharge zone using an optical spectrometer (Maya2000Pro, Ocean Optics).

3. Results and discussion

With Ar addition (5-50 mL/min, respectively) to the CO₂/H₂ feed, the total flow rate was increased to 55-100 mL/min, respectively. Regarding the absolute CO₂ conversion and CH₄ selectivity, they dropped in the experiments with Ar addition at ≥10 mL/min though the concentrations of the energetic species (i.e., CO/CO₂⁺/CO₂/CH) were improved (by OES). Such adverse effect due to Ar addition was more significant on CO₂ conversion than CH₄ selectivity. Especially in the experiment with 50 mL/min Ar addition (corresponding to a total 100 mL/min feed flow rate), the measured CO₂ conversion is 49.0%, being significantly lower than that in the Ar-free experiment (CO₂ conversion = ~71%, Figure 1a). Comparatively, CH₄ selectivity dropped by ~20%. The adverse effect also led to the decrease in the CH₄ production rate (Figure 1b), possibly due to the reduction in residence time due to the increase in the total flow rate, which was estimated at about 0.49 s at a total flowrate of 50 mL/min and halved at 100 mL/min. To investigate the effect of residence time on the system, the discharge length of the systems was extended from 25 mm to 35 mm (with the constant loading of the catalyst), corresponding to the increase in the residence time from 0.49 s to 0.69 s. Figure 2 shows that an increase in residence time

under NTP conditions could improve the system performance considerably at same or similar applied voltages. Increasing the residence time extends the duration that reactants stay within the reaction zone, which enhances the likelihood of CO₂/H₂ to be activated by gas discharge. Additionally, at a comparable discharge power, an increase in discharge volume means a larger discharge space. This expansion causes the electric field to cover a broader area, which may lead to a decrease in the average electric field intensity across the discharge region. A reduced electric field intensity favors the vibrational excitation of CO₂ molecules, preventing the direct dissociation of CO₂ (to CO species) that occurs at high electric field strengths [5]. The vibrationally excited CO₂ could benefit the energy efficiency (Figure 2b).

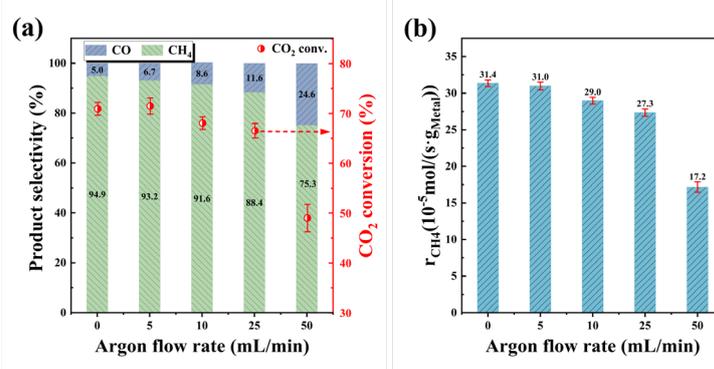


Figure 1. Effect of Ar addition on the performance of NTP catalytic CO₂ hydrogenation over the Ni catalyst at 11 kV and 7.4 kHz (a) CO₂ conversion and CH₄ selectivity and (b) CH₄ production rate (all experiments were performed at the constant H₂ and CO₂ flow rate of 40 and 10 mL/min, respectively).

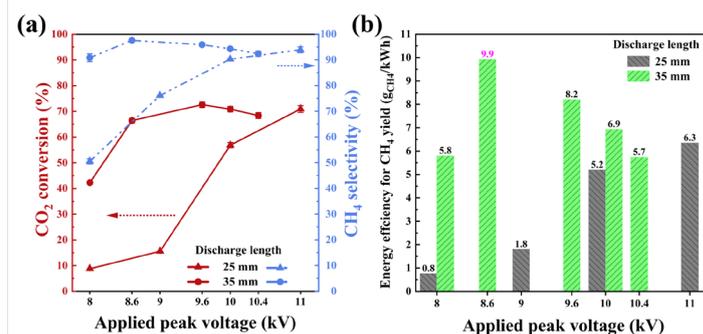


Figure 2. Effect of discharge length on performance of NTP catalysis CO₂ hydrogenation over the Ni catalyst (a) CO₂ conversion and CH₄ selectivity; (b) Energy efficiency (based on CH₄ yield) (experimental conditions: total flow rate of 50 mL/min, CO₂/H₂ ratio = 1:4, applied peak voltage of 8–11 kV, frequency of 7.4 kHz).

4. Conclusions

Findings of the study show the significance of reaction engineering study to improve plasma catalysis, helping the performance optimization especially improving the system energy efficiency, which could benefit the development of the hybrid technology towards the practical applications.

References

The reference format is provided below [1 – 3]. [Times New Roman 10].

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Keywords

Nonthermal plasma; catalysis; CO₂ hydrogenation; reaction engineering