

Supplementary Material

Dry reforming of methane in gliding arc plasma: Bridging thermal and post-plasma catalysis

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Section S1. Calculation of CO₂ and CH₄ conversion and product distribution DRM in the thermal reactor

CO₂ and CH₄ conversion and product distribution were determined at each temperature by the average of four different analyses following eq. S1 and eq. S2, respectively. H₂ and CO yield were calculated as defined in eq. S3 and eq S4, respectively.

$$X_{CO_2}(\%) = \left(\frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \right) \cdot 100 \quad (\text{eq. S1})$$

$$X_{CH_4}(\%) = \left(\frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \right) \cdot 100 \quad (\text{eq. S2})$$

$$Y_{H_2}(\%) = \left(\frac{F_{H_2}}{2F_{CH_4,in}} \right) \cdot 100 \quad (\text{eq. S3})$$

$$Y_{CO}(\%) = \left(\frac{F_{CO}}{F_{CO_2,in} + F_{CH_4,in}} \right) \cdot 100 \quad (\text{eq. S4})$$

Where $F_{i,in}$ or $F_{out,in}$ is the flow rate of each component in the reactants and products.

Plasma-assisted DRM performance and energy metric formulae

As the DRM reaction produces four molecules, starting from two molecules (in case of full conversion; cf Eq. 1 in the main paper), it leads to gas expansion. This needs to be accounted for, by means of the so-called flux ratio, as explained in detail by Wanten et al.¹. In the cases with excessive H₂O production and negligible solid carbon deposition (i.e. 10 – 30 % CH₄) the carbon balance is used to determine the volumetric outflow (Q_{out}). In the cases with excessive solid carbon production and negligible H₂O (i.e. 40 – 50 % CH₄) the oxygen balance is used to determine the flux ratio.

In the cases utilising the carbon balance to determine volumetric flow (L min⁻¹) from the reactor, the formula is defined as:

$$Q_{out} = \frac{(Q_{in} \cdot \gamma_{CO_2}^{in} + Q_{in} \cdot \gamma_{CH_4}^{in})}{(\gamma_{CO_2}^{out} + \gamma_{CO}^{out} + \gamma_{CH_4}^{out})} \quad (\text{eq. S5})$$

Where Q_{in} is the volumetric flow rate at the inlet ($L \text{ min}^{-1}$) and γ is the fraction of the component in the inlet or outlet indicated in the subscript and superscript, respectively.

In the cases utilising the oxygen balance to determine Q_{out} , the formulae are similar as that used by Zhang et al.² and in our previous work:³

$$Q_{out} = \frac{2 \cdot Q_{in} \cdot \gamma_{CO_2}^{in}}{(2 \cdot (\gamma_{CO_2}^{out} + \gamma_{O_2}^{out}) + \gamma_{CO}^{out})} \quad (\text{eq. S6})$$

The absolute conversion (X^{abs} , %) of component i is defined as:

$$X^{abs} = \frac{(Q^{in} \cdot y_i^{in}) - (Q^{out} \cdot y_i^{out})}{Q^{in} \cdot y_i^{in}} \cdot 100 \quad (\text{eq. S7})$$

where y_i^{in} is the inlet fraction of component i and y_i^{out} is the fraction of component i detected in the effluent. The effective conversion (X^{eff} , %) of component i is defined as:

$$X^{eff} = X_i^{abs} \cdot y_i^{in} \quad (\text{eq. S8})$$

Using this definition, the total conversion (X^{tot} , %) is calculated according to the summation of the effective conversions:

$$X^{tot} = \sum_i^n X_i^{eff} \quad (\text{eq. S9})$$

The production rate of CO and H₂ (PR , $\text{mol mol}_{Ni}^{-1} \text{ min}^{-1}$) per mole of Ni loading can be calculated by:

$$PR = \frac{Q_{out} \cdot \gamma_i^{out} \cdot m_{cat} \cdot \alpha_{Ni}}{V_m \cdot M_{Ni}} \quad (\text{eq. S10})$$

Where m_{cat} is the mass of catalyst loaded into the post-plasma catalyst bed (8 g), α_{Ni} is the weight loading fraction of Ni, and M_{Ni} is the molar mass of Ni ($58.693 \text{ g mol}^{-1}$).

The average plasma-deposited power (P , kW) is calculated by averaging instantaneous power measurements (three per 10 min period):

$$P = \frac{1}{n} \cdot \sum_{i=1}^n V_{plasma_i} \cdot I_{plasma_i} \quad (\text{eq. S11})$$

Where n is the number of points recorded, V_{plasma_i} is the measured voltage drop across the plasma (kV) and I_{plasma_i} is the measured current (A) calculated by:

$$V_{plasma_i} = \frac{V_{shunt_i}}{R_{shunt_i}} \quad (\text{eq. S12})$$

Where V_{shunt_i} is the voltage drop measured across the shunt resistor (V) and R_{shunt_i} is the known shunt resistance (2 Ω).

The specific energy input (SEI , kJ L^{-1}) is the ratio of power to flow rate, defined as:

$$SEI = \frac{P}{Q^{in}} \cdot 60 \quad (\text{eq. S13})$$

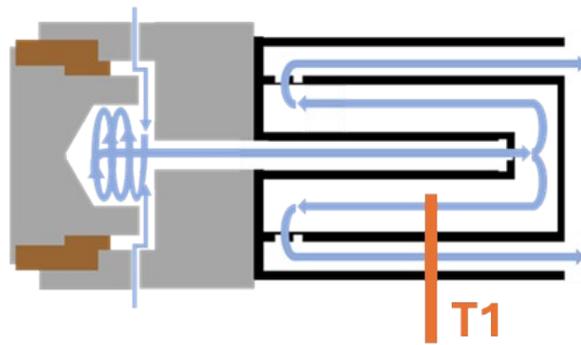
Where 60 is the conversion factor for seconds to minutes. SEI unit conversion between kJ L^{-1} , kJ mol^{-1} and eV/molecule have been defined previously.²

The energy cost (EC) is used as the key energy metric describing the system. EC (MJ mol^{-1}) combines the conversion and SEI parameters into a quantifiable measure of the energy expenditure of the process and is defined as:

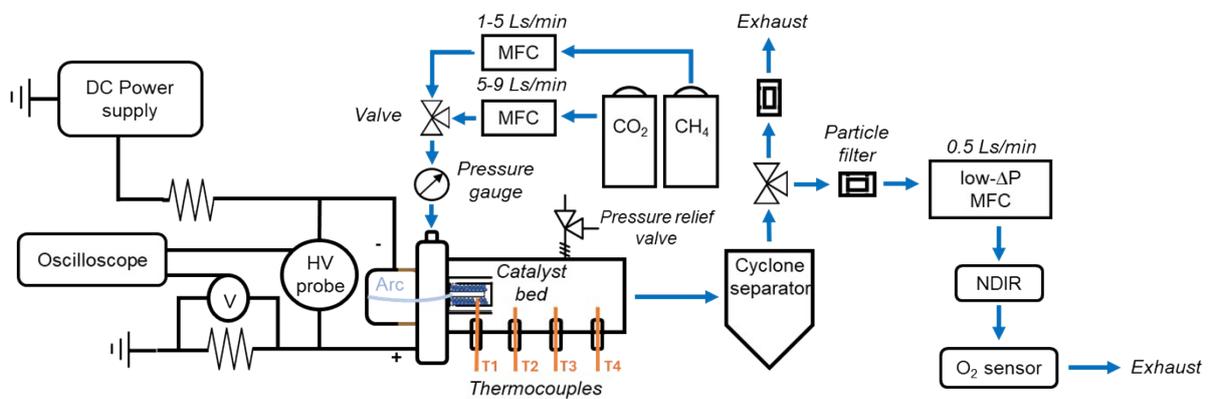
$$EC = \frac{SEI}{(X^{tot} / 100)} \quad (\text{eq. S14})$$

Where SEI is defined in MJ mol^{-1} and the denominator 100 (%) is used to obtain the total conversion as a fraction.

(a)



(b)



(c)

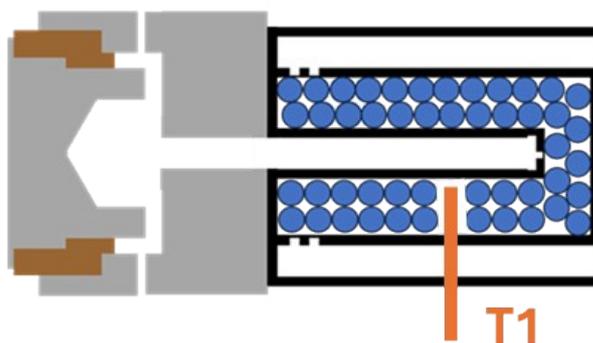


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Table S1. Average inlet pressure (bar) for each inlet CH₄ fraction (vol%) at a fixed total flow rate of 10 L min⁻¹, without and with packed catalyst.

	Without catalyst	With catalyst
CH ₄ fraction (vol%)	Average inlet pressure (bar)	Average inlet pressure (bar)
10	1.35 ± 0.07	1.41 ± 0.03
20	1.37 ± 0.05	1.42 ± 0.03
30	1.38 ± 0.02	1.39 ± 0.04
40	1.33 ± 0.06	1.41 ± 0.09
50	1.33 ± 0.02	1.53 ± 0.24

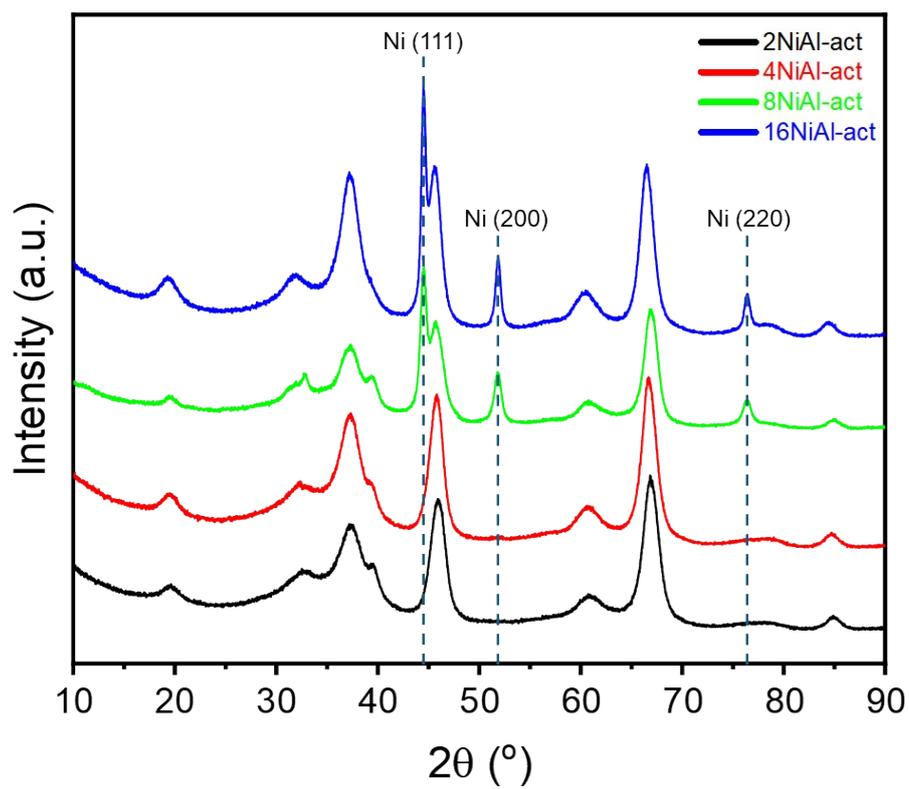


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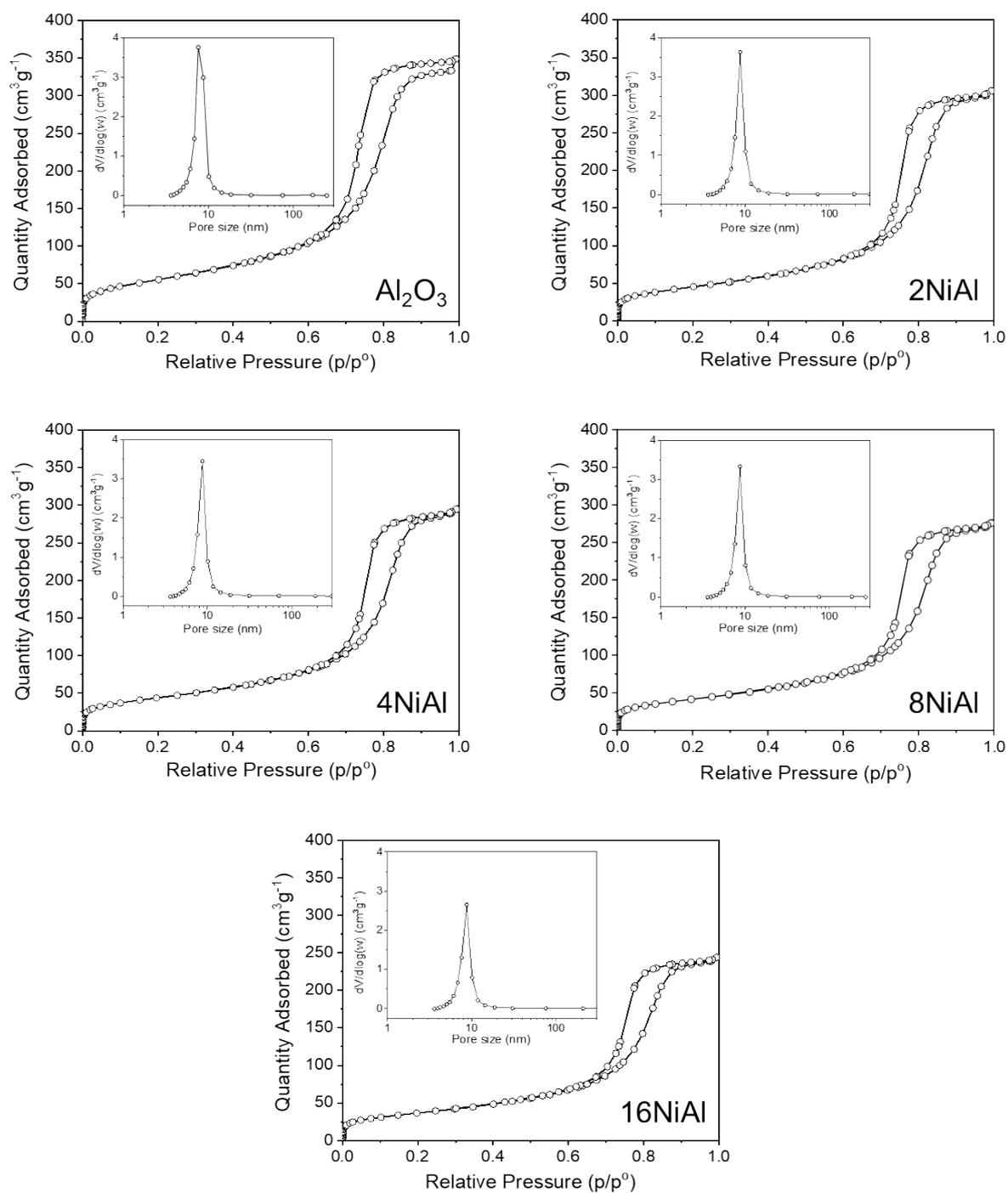


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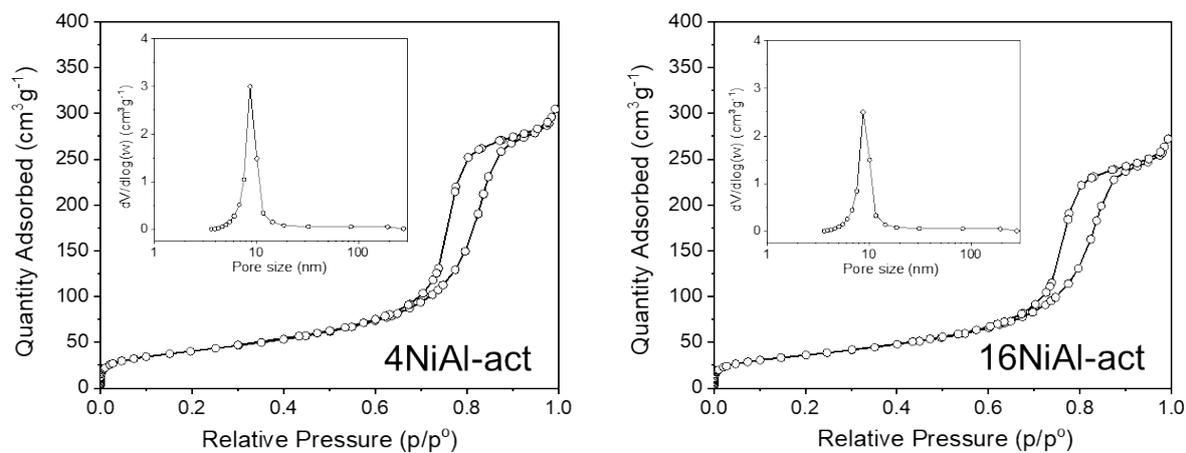


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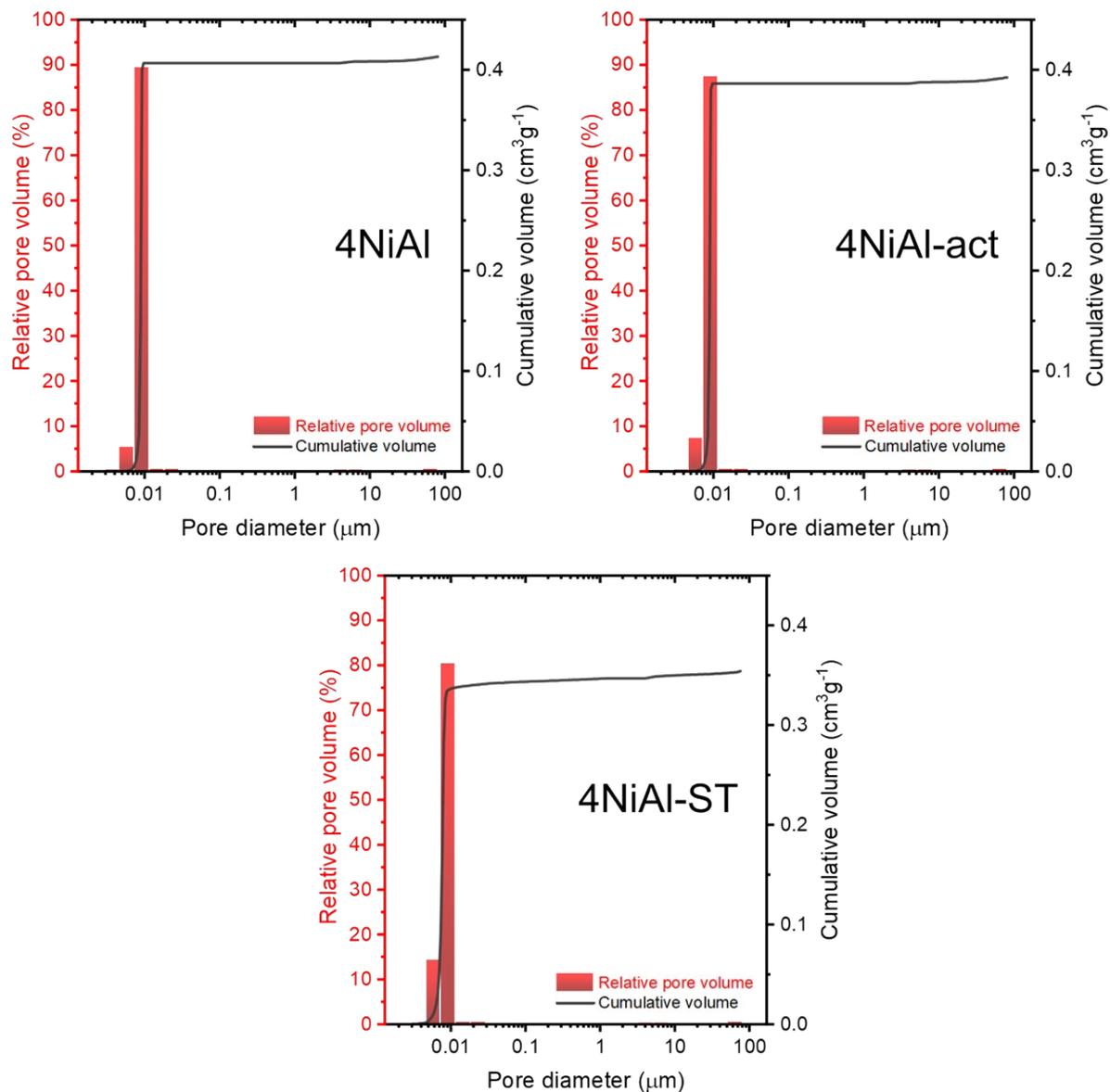


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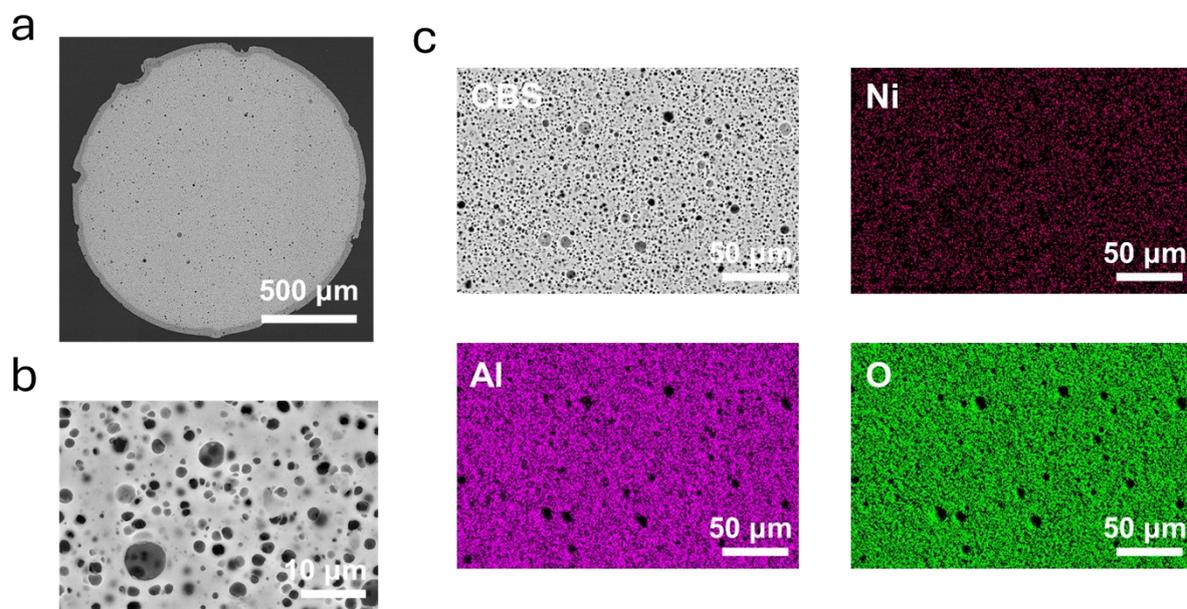


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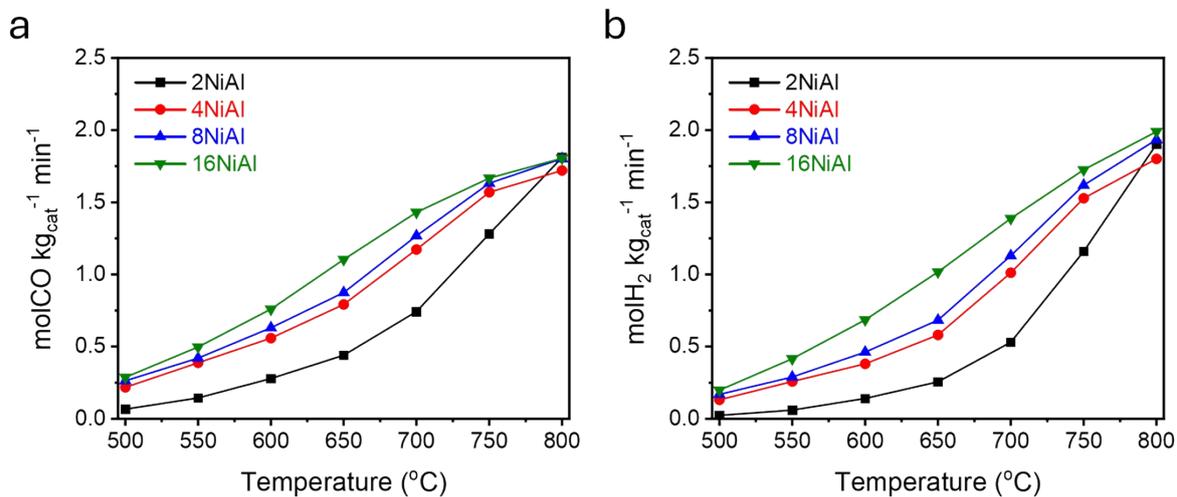


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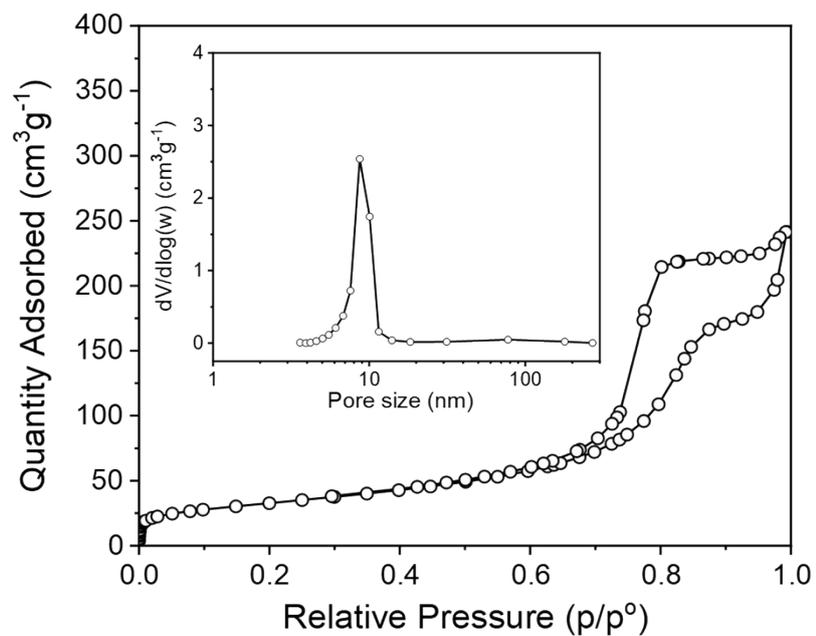


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CH ₄ fraction (vol%)	Set current (mA)	Without catalyst		With catalyst	
		Average plasma voltage (kV)	Average plasma power (kW)	Average plasma voltage (kV)	Average plasma power (kW)
10	650	1.34 ± 0.032	0.89 ± 0.021	1.29 ± 0.038	0.85 ± 0.025
20	650	1.53 ± 0.011	1.01 ± 0.007	1.44 ± 0.018	0.95 ± 0.012
30	650	1.70 ± 0.005	1.12 ± 0.003	1.60 ± 0.012	1.06 ± 0.008
40	690	1.76 ± 0.024	1.16 ± 0.016	1.67 ± 0.019	1.11 ± 0.013
50	690	1.78 ± 0.051	1.18 ± 0.002	1.69 ± 0.004	1.12 ± 0.004

References

1. B. Wanten, R. Vertongen, R. De Meyer and A. Bogaerts, *Journal of Energy Chemistry*, 2023, **86**, 180-196.
2. H. Zhang, Q. Tan, Q. Huang, K. Wang, X. Tu, X. Zhao, C. Wu, J. Yan and X. Li, *ACS Sustainable Chemistry & Engineering*, 2022, **10**, 7712-7725.
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