



Cite this: *EES Catal.*, 2025,  
3, 1087

## Dry reforming of methane in gliding arc plasma: bridging thermal and post-plasma catalysis†

Colin O'Modhrain,<sup>ib ‡\*ab</sup> Arturo Pajares,<sup>ib ‡\*c</sup> Eduardo Coutino-Gonzalez,<sup>ib c</sup>  
 Yoran de Vos,<sup>c</sup> Pablo Guardia,<sup>ib d</sup> Yuri Gorbaney,<sup>ib ab</sup> Bart Michielsens<sup>ib c</sup> and  
 Annemie Bogaerts<sup>ib ab</sup>

This study compares thermal and post-plasma catalysis for dry reforming of methane (DRM) using nickel–alumina catalyst spheres. The optimum catalyst loading was first determined by thermo-catalytic performance testing and characterization. The selected catalyst spheres (4 wt% Ni loading) were introduced to a novel post-plasma-catalytic bed, designed to utilize the sensible heat from the plasma reactor and boost the DRM reaction without additional heating. A parametric scan of inlet CH<sub>4</sub> fractions (10–50 vol%) consistently shows improved CH<sub>4</sub> conversion in the presence of a catalyst. The CO and H<sub>2</sub> production rates reach peak values of ca. 24.4 mol mol<sub>Ni</sub><sup>−1</sup> min<sup>−1</sup> with 40 vol% CH<sub>4</sub> at the inlet, at a minimum energy cost (EC) of around 0.24 MJ per mol of reactant mixture. Interestingly, the addition of catalyst does not benefit the EC, but instead results in an improved syngas (H<sub>2</sub>/CO) ratio for 10–30 vol% CH<sub>4</sub>. In addition, a long-run post-plasma-catalytic test (6 h) demonstrates stable conversion and syngas ratio values. The EC obtained in this study is by far the lowest reported in post-plasma-catalytic DRM to date, and the insulated bed design reduces the heat loss from the bed and enables a more stable output. The successful coupling of a thermo-catalytic catalyst selection process with implementation in a post-plasma-catalytic bed demonstrates the coupling potential that can be realized between both research domains.

Received 8th March 2025,  
Accepted 29th May 2025

DOI: 10.1039/d5ey00067j

[rsc.li/eescatalysis](https://rsc.li/eescatalysis)

### Broader context

The global shift toward carbon-neutral technologies has intensified interest in dry reforming of methane (DRM)—a process that valorises biogas, by converting methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) into syngas (H<sub>2</sub> and CO), a crucial feedstock for fuels and chemicals. While DRM offers a sustainable alternative to fossil-based syngas production, its practical implementation is hindered by high energy requirements and catalyst deactivation from solid carbon deposition. Our research addresses this challenge with a combined experimental approach of thermal and post-plasma catalysis, where plasma activates reactant gases and generates heat. We developed an optimised Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, first validated under thermal conditions and then incorporated into an insulated post-plasma catalytic bed. The novel bed design ensures a more homogeneous bed temperature, which is beneficial for the endothermic DRM reaction. Our study demonstrates the lowest energy cost for post-plasma-catalytic DRM reported to date, showcasing a pathway toward more efficient DRM technology. By demonstrating the benefits of catalyst pre-screening for post-plasma applications, we highlight a viable pathway for cleaner syngas production, supporting broader efforts toward energy efficiency and carbon reduction in the chemical sector.

## 1. Introduction

In the context of the current global energy landscape, sustainable fuel alternatives with a zero or negative CO<sub>2</sub> cycle are highly desirable. Dry reforming of methane (DRM) is a process that converts methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) into syngas (H<sub>2</sub> and CO), a valuable feedstock for fuel production and chemical synthesis (eqn (1)).<sup>1–3</sup> This process holds significant potential for mitigating greenhouse gas emissions by utilizing two major contributors to global warming, as well as for biogas valorisation. However, conventional thermal DRM

<sup>a</sup> Research group PLASMAN, Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium.  
E-mail: [colin.omodhrain@uantwerpen.be](mailto:colin.omodhrain@uantwerpen.be)

<sup>b</sup> Electrification Institute, University of Antwerp, Olieweg 97, 2020 Antwerp, Belgium

<sup>c</sup> Materials & Chemistry, Flemish Institute for Technological Research (VITO NV), Boeretang 200, 2400 Mol, Belgium. E-mail: [arturo.pajares@vito.be](mailto:arturo.pajares@vito.be)

<sup>d</sup> Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Bellaterra, 08193 Barcelona, Spain

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5ey00067j>

‡ These authors contributed equally.



operates at high temperatures (typically above 750 °C) and is prone to catalyst deactivation due to carbon deposition.<sup>4–6</sup>



Nickel-based catalysts are widely used in DRM due to their high catalytic activity and low industrial cost. However, carbon deposition hinders large-scale applications.<sup>7</sup> The size and dispersion of active metal particles significantly influence catalytic performance, with smaller Ni particle sizes effectively preventing carbon formation.<sup>8</sup> Al<sub>2</sub>O<sub>3</sub> is a commonly used support in industrial catalysts, offering a large specific surface area and excellent thermal stability.<sup>9</sup> Ni serves as the active metal, facilitating the dissociation of CH<sub>4</sub> and CO<sub>2</sub>, while the structured Al<sub>2</sub>O<sub>3</sub> support enhances dispersion and mitigates sintering at high temperatures. However, in conventional thermal DRM, reaction temperatures above 750 °C are required to achieve high conversion rates. This leads to high energy consumption and potential catalyst deactivation over time, despite the generally reduced sintering mentioned earlier. The integration of plasma with thermal catalysis may enhance performance by utilizing plasma-generated heat and reactive species in a post-plasma-catalytic system.

As electrified processes gain traction as alternatives to conventional thermal catalysis, plasma (a partially or fully ionised gas with collective properties) emerges as a low-inertia technology, fully compatible with intermittent renewable energy sources.<sup>10,11</sup> Plasma catalysis can enhance conversion and selectivity in plasma-based processes by either incorporating a catalyst within the discharge zone (in-plasma catalysis, IPC) or placing it downstream from the plasma (post-plasma catalysis, PPC).

IPC benefits from short-lived reactive species in the catalyst region,<sup>12</sup> but requires low gas temperatures, such as those in dielectric barrier discharge (DBD) reactors, to prevent catalyst degradation.<sup>13,14</sup> Moreover, introducing materials into the discharge zone can alter plasma characteristics,<sup>15,16</sup> necessitating further study to optimize the coupled performance and achieve the potential synergy. In PPC, the catalyst is positioned downstream, allowing for higher temperatures of the plasma itself, because the catalyst is spatially separated from it, thus avoiding catalyst damage.<sup>17,18</sup> This setup is often used with higher-temperature plasmas, such as (rotating) gliding arc ((R)GA) or microwave (MW) reactors, where excess plasma heat activates thermal catalysts. Unlike IPC, where the effects of plasma on catalyst and vice versa are vast and go beyond the conventional catalytic paradigm,<sup>16,17</sup> PPC provides a direct link to thermal catalysis, leveraging extensive knowledge from this field. PPC has been explored in various reactor setups and reactions, including NH<sub>3</sub> cracking, CO<sub>2</sub> splitting, CH<sub>4</sub> pyrolysis, and dry, bi- or oxidative reforming of CH<sub>4</sub>.<sup>19–22</sup>

PPC-DRM research has spanned multiple reactor designs.<sup>23–29</sup> Allah and Whitehead<sup>25</sup> improved the CO<sub>2</sub> and CH<sub>4</sub> conversion using a planar GA reactor with a NiO/Al<sub>2</sub>O<sub>3</sub> catalyst bed. Li *et al.*<sup>21</sup> employed a rotating GA (RGA) reactor with dual CH<sub>4</sub> injection and a Ni/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, achieving an H<sub>2</sub>/CO ratio of 1, which is higher than most reports, but still below the ideal ratio for

methanol or dimethyl ether synthesis.<sup>30</sup> Their setup maintained the catalyst bed at 850 °C by encapsulating the reactor exhaust in a tubular furnace, which inherently introduces extra energy costs as an external heat source. Martin-del-Campo *et al.*<sup>28</sup> investigated Ni (15–30 wt%) on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> supports in an RGA reactor with a spouted catalyst bed, which improved heat transfer. However, the presence of a catalyst in the discharge zone reduced the conversion due to disruption of the arc. In this regard, the authors found that a more stable discharge was achieved with the Al<sub>2</sub>O<sub>3</sub>-supported catalyst, and that the introduction of catalysts reduced the formation of soot and coke.

Xu *et al.*<sup>29</sup> recently tested a Ni/LDH catalyst diluted with Al<sub>2</sub>O<sub>3</sub> beads downstream from a gliding arc plasmatron (GAP) reactor. By heavily diluting the CO<sub>2</sub>/CH<sub>4</sub> feed with N<sub>2</sub> (~80%), they achieved equimolar conversion without carbon deposition (*i.e.*, soot/coke). A comparison between a tray-like catalyst bed and a tubular catalyst bed revealed much improved conversion of both CO<sub>2</sub> and CH<sub>4</sub> in the tubular catalyst bed, which the authors attribute to a higher bed temperature. They reported an energy cost (EC) of 4.3 kJ L<sup>−1</sup>, which was the lowest compared to several other works of literature, albeit this value accounted only for the effective conversion of CO<sub>2</sub> rather than the total conversion (see the discussion below, in Section 3.3.1, for details).

Evidently, studies have demonstrated that placing a Ni-based catalyst bed after the plasma zone improves CH<sub>4</sub> and CO<sub>2</sub> conversion by ensuring unreacted feed gases undergo further catalytic conversion. Additionally, optimizing the position of the Ni/Al<sub>2</sub>O<sub>3</sub> spheres after the plasma reactor can enhance heat transfer, reducing the need for external heating. This integration aligns with the goal of developing a fully electrically-driven DRM process, where plasma not only activates reactants but also preheats the catalyst, creating a self-sustaining reaction environment. To overcome the limitations of both standalone plasma and thermal catalysis, rationally designed structured catalysts play a crucial role in bridging the gap between these two approaches, paving the way for a more efficient and scalable DRM technology.

In this study, we implement a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst downstream from a GAP plasma reactor. The developed catalyst is first screened and characterised using thermal DRM to determine the optimum Ni loading. Following this, the selected catalyst is introduced into a specially designed post-plasma insulated bed, previously developed in our group for post-CO<sub>2</sub> plasma carbon beds, where we achieved a homogeneous bed temperature without external heating.<sup>31</sup> Importantly, unlike prior studies,<sup>23,24,28,29</sup> our plasma experiments use a pure CO<sub>2</sub>/CH<sub>4</sub> mixture (without N<sub>2</sub> or noble gas dilution), reducing costs associated with gas separation and bringing the process closer to industrial relevance.

## 2. Experimental

### 2.1. Catalyst preparation

Commercial Al<sub>2</sub>O<sub>3</sub> spheres (Sasol,  $S_{\text{BET}} = 200 \text{ m}^2 \text{ g}^{-1}$  and  $\phi = 1 \text{ mm}$ ) were used as the support material for a series of Ni-based catalysts. The diameter was selected to reduce the



pressure drop across the catalyst bed.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma Aldrich, 99%) was used as Ni precursor in aqueous solution. Different Ni loadings of 2–16 wt% were prepared using incipient wetness impregnation. The samples were henceforth named according to the Ni loading, *i.e.*, 2NiAl (2 wt% Ni), 4NiAl (4 wt% Ni), 8NiAl (8 wt% Ni) and 16NiAl (16 wt% Ni). The impregnated samples were dried overnight and calcined at 800 °C for 2 h under air to form the  $\text{NiAl}_2\text{O}_4$  phase. For the plasma-assisted DRM tests, 100 g of 4NiAl were prepared and activated *ex situ* using a  $\text{H}_2/\text{N}_2$  (50/50) flow of 100 mL  $\text{min}^{-1}$  at 750 °C for 3 h before testing.

## 2.2. Catalyst characterization

X-ray powder diffraction (XRPD) was performed at room temperature over a  $2\theta$  range of 4°–100° using a PANalytical X'Pert PRO MPD diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Phase identification was conducted by comparing diffraction patterns with the ICDD Powder Diffraction database. Ni content was quantified using a Niton XL3t-Goldd XRF Analyzer (Thermo Scientific). X-ray photoelectron spectroscopy (XPS) measurements were carried out at  $5 \times 10^{-10}$  mbar using a SPECS PHOIBOS 150 hemispherical analyser (SPECS GmbH, Berlin, Germany) with monochromatic Al  $\text{K}\alpha$  radiation (1486.74 eV) at 300 W. Spectra were calibrated using the C 1s peak as reference.

$\text{N}_2$  adsorption–desorption isotherms were measured at –196 °C using an Autosorb iQ2 MP instrument. Prior to testing, the samples were degassed at 200 °C for 16 h to remove adsorbed water. The specific surface area ( $S_{\text{BET}}$ ) was determined using multi-point Brunauer–Emmett–Teller (BET) analysis, while pore size distribution was calculated *via* the Barrett–Joyner–Halenda (BJH) method. Hg intrusion porosimetry was conducted with a Thermo–Finnigan porosimeter, from vacuum to 0.2 MPa, followed by measurements between 1 and 200 MPa. Morphological homogeneity and infill patterns of printed structures were analysed *via* optical microscopy (OM), using a Zeiss Discovery V12 stereomicroscope. Scanning electron microscopy (SEM), cross-section analysis, and energy dispersive X-ray (EDX) mappings were performed on a FEI Nova NanoSEM 450 (up to 20 keV) equipped with a Bruker QUANTAX 200 EDX system and XFlash 6160 SDD detector. Cross-section SEM samples were cut at the midpoint and embedded under vacuum in epoxy resin (EpoFix Resin/Hardener).

$\text{H}_2$ -temperature programmed reduction ( $\text{H}_2$ -TPR) was conducted using a micromeritics 3Flex system. Samples were pretreated at 90 °C under Ar, cooled to room temperature, then exposed to a  $\text{H}_2/\text{Ar}$  (10% v/v) flow while heating to 1000 °C at 10 °C  $\text{min}^{-1}$ . The TCD signal was recorded during reduction. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449 F3 Jupiter instrument, where 100 mg of sample was heated from 40 to 1000 °C (10 °C  $\text{min}^{-1}$ ) under air flow.

## 2.3. Thermal catalytic DRM setup

Preliminary thermal DRM tests were conducted in a quartz tube fixed-bed reactor (i.d. = 1.1 cm) placed inside a Carbolite® furnace and connected to a gas chromatograph (Trace 1300 GC, Thermo Fisher Scientific) equipped with two TCDs and one FID

detector. A 0.75 g sample of  $\text{Ni}/\text{Al}_2\text{O}_3$  spheres was positioned at the reactor centre, with a thermocouple in direct contact. Prior to catalytic testing, *in situ* pretreatment was performed under a 100 mL  $\text{min}^{-1}$  flow rate of  $\text{H}_2/\text{N}_2$  (1/1 molar ratio) at 750 °C for 1 h. The temperature was then reduced to 500 °C under the same gas flow rate. The sample was subsequently exposed to a reactant gas mixture of  $\text{CO}_2/\text{CH}_4/\text{N}_2$  (1/1/3) at a total inlet flow rate of 100 mL  $\text{min}^{-1}$ , corresponding to a gas hourly space velocity (GHSV) of 8000 mL  $\text{g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . The catalytic performance was evaluated over a temperature range of 500–800 °C at 0.1 MPa. A long-term catalytic test (5 days) was conducted for the most efficient catalysts at 700 °C, using again 0.75 g of catalyst, 0.1 MPa, and the same GHSV of 8000 mL  $\text{g}_{\text{cat}}^{-1} \text{ h}^{-1}$  with the same reactant gas mixture ( $\text{CO}_2/\text{CH}_4/\text{N}_2 = 1/1/3$ ). After the tests, samples were thoroughly characterized, and product analysis was performed online using a gas chromatograph. CO and  $\text{H}_2$  were the main observed products, with trace amounts of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  detected.

## 2.4. Plasma-catalytic DRM setup

Post-plasma catalysis tests were conducted using a gliding arc plasmatron (GAP) reactor, as described in previous studies.<sup>29,32,33</sup> The Ni-based catalyst (4NiAl) was loaded into a bed attached to the outlet of the GAP reactor, with 8 g used in each experiment. The bed design forces the high-temperature effluent from the plasma reactor through the catalyst and around the bed in an insulating manner (see ESI† Fig. S1a), thus ensuring better heat retention and a more consistent bed temperature throughout the whole volume. The extended anode ensures the catalyst is positioned sufficiently far from the plasma to avoid direct contact with it and thus thermal-associated catalyst damage. In addition, this bed feature reduces the likelihood of plasma-generated reactive species (*i.e.*, radicals/ions) from reaching the catalyst, as the lifetime of such species at atmospheric pressure is short. Therefore, the plasma effect is solely to thermally activate the catalyst. Benchmark tests were performed with an empty catalyst bed. A schematic of the reactor setup with the insulated catalyst bed is shown in Fig. S1b (ESI†). Each experiment was run in triplicate for 1 h. Additionally, one long run of 6 h was conducted using the 30 vol%  $\text{CH}_4$  fraction, to demonstrate the capability of the system for extended coupled plasma-catalytic performance.

$\text{CO}_2$  and  $\text{CH}_4$  (99.999% and 99.995%, Air Liquide) were supplied to a single gas inlet connected to a swirl ring containing six tangential inlets, and the flow rate was controlled using mass flow controllers (MFCs) (Bronkhorst, F-201AV/F-201CV). The unit of flow rate was set according to the Bronkhorst standard litre per minute, which aligns with the standard EU definition taken at 20 °C and 0.1 MPa (molar volume = 24.06 L  $\text{mol}^{-1}$ ). The total flow rate was set to 10 L  $\text{min}^{-1}$ , while the  $\text{CO}_2/\text{CH}_4$  ratio was varied from 90/10 vol% to 50/50 vol%. The GHSV was fixed at 75 000 mL  $\text{g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . In all post-plasma catalysis tests, no diluting gas was present. The inlet pressure was monitored throughout with a pressure gauge, with the average readings shown in ESI† (Table S1). The maximum recorded pressure difference between the benchmark and plasma-catalytic experiments was approximately 0.2 bar. The outlet



Reactor performance was assessed using formulae previously defined by Wanten *et al.*<sup>36</sup> This study evaluates performance in terms of absolute, effective, and total conversion. To quantify the energy performance, we define the EC of the process in relation to the total conversion. It is important to use the total conversion in this calculation for multi-component mixtures, where more than one reactant is being converted (as is the case with DRM). All formulae, including the flux ratio considerations (accounting for gas expansion, inherent to DRM), are provided in the ESI,<sup>†</sup> section S1.



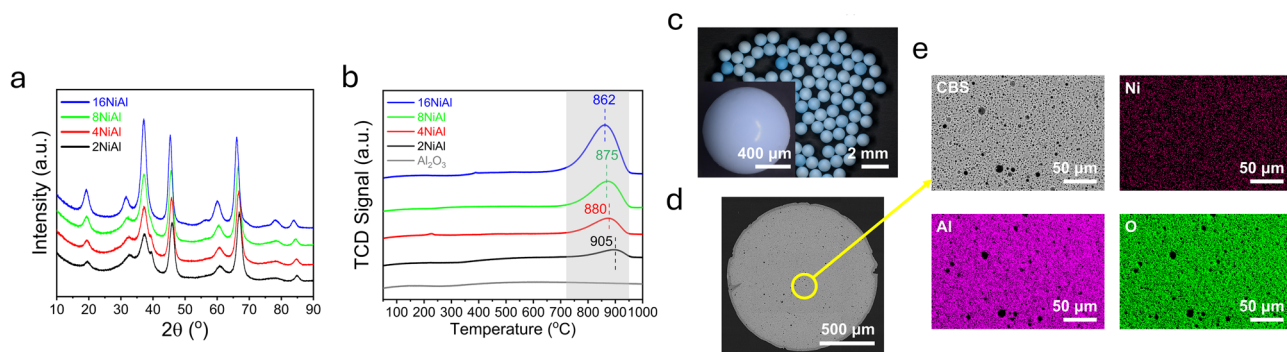


Fig. 1 Characterization of NiAl samples. (a) XRD patterns and (b)  $H_2$ -TPR of NiAl samples. (c)–(e) Textural characterization of 4NiAl: (c) OM, (d) cross-sectional SEM images and (e) EDX mapping.

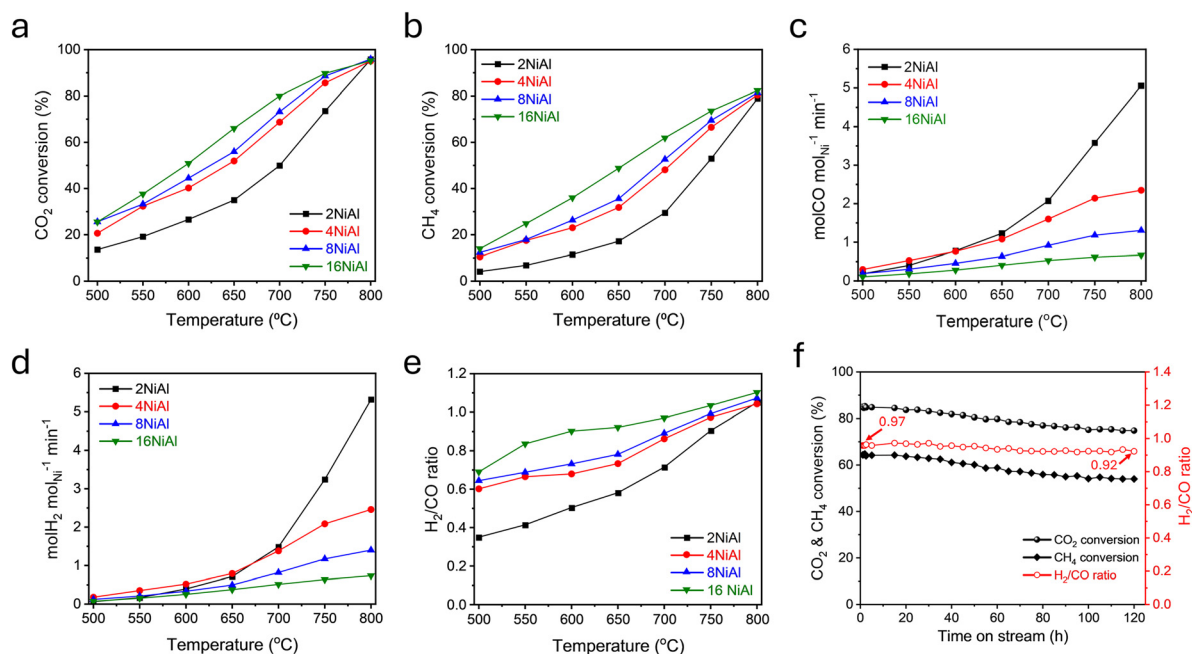


Fig. 2 Catalytic behaviour of the NiAl samples in the thermal DRM. (a)  $CO_2$  conversion, (b)  $CH_4$  conversion, (c) CO production, (d)  $H_2$  production, and (e)  $H_2/CO$  molar ratio, for the four different NiAl samples, and (f) stability test of the 4NiAl sample at 700 °C. Reaction conditions: pressure = 0.1 MPa,  $CO_2/CH_4/N_2 = 1/1/3$ , GHSV = 8000 mL  $g_{cat}^{-1} h^{-1}$ ,  $m_{cat} = 0.75$  g. Pre-treatment conditions: pressure = 0.1 MPa,  $H_2/N_2 = 1/1$ ,  $T = 750$  °C.

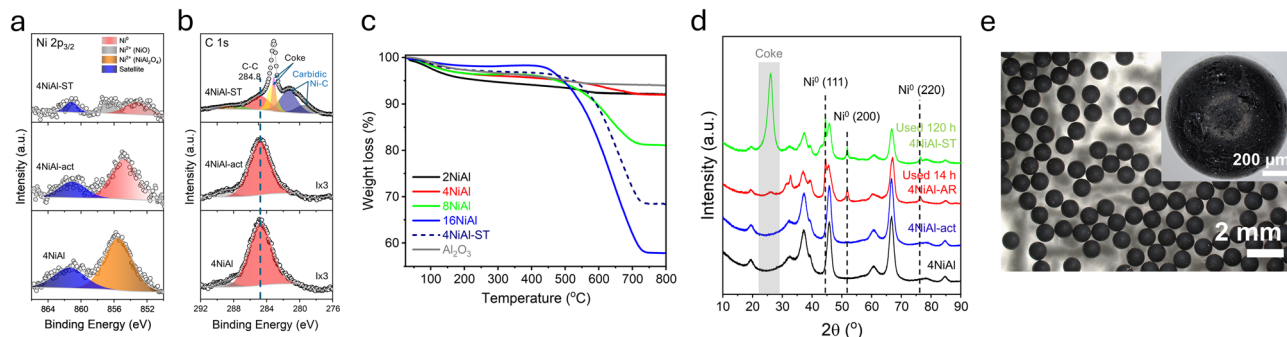
XPS analysis of 4NiAl revealed a feature corresponding to  $Ni^{2+}$  in  $NiAl_2O_4$  within the  $Ni\ 2p_{3/2}$  core level spectrum (Fig. 3a).<sup>40</sup> After activation (4NiAl-act), a shift to lower binding energy suggested  $Ni^0$  formation on the surface.<sup>41</sup> The slightly higher binding energy of  $Ni^0$  compared to reported values indicated strong Ni-support interactions, aligning with the  $H_2$ -TPR results.<sup>38,39</sup> No differences were observed in the C 1s core level spectrum (Fig. 3b).

### 3.2. Thermal catalytic DRM tests

Thermal catalytic tests showed that all NiAl samples, prior to activation, were active under the reaction conditions.  $CO_2$  and  $CH_4$  conversion increased with temperature, reaching equilibrium conversion values at 800 °C (95% and 82%, respectively) for all samples (Fig. 2a and b). Among them, 16NiAl exhibited

the highest performance per mass of catalyst loading (Fig. S7, ESI†). However, when syngas production ( $CO + H_2$ ) was normalized to Ni loading (Fig. 2c and d), 2NiAl displayed the highest catalytic activity, attributed to its smaller Ni crystallites and greater Ni surface exposure.

The syngas ratio ( $H_2/CO$ ) increased with both temperature and Ni loading, exceeding 1.0 for all samples at 800 °C (Fig. 2e). This suggests that higher Ni loadings enhance  $CH_4$  decomposition, which benefits  $H_2$  production, but also having the drawback of accelerated carbon formation. For stability testing at 700 °C over 120 h, 4NiAl was selected due to its higher catalytic activity compared to 2NiAl and lower coke formation than 8NiAl and 16NiAl (Fig. S7 (ESI†) and Fig. 3c). The large coke formation leads to catalyst deactivation and increased reactor pressure drop. The stability test showed a slight deactivation after 120 h,



**Fig. 3** Characterization of used NiAl catalysts. (a) Ni 2p<sub>3/2</sub> and (b) C 1s XPS spectra of fresh (4NiAl), activated (4NiAl-act) and used samples after stability test at 700 °C (4NiAl-ST). (c) TGA of used NiAl samples under air. (d) XRD patterns of 4NiAl, 4NiAl-act, 4NiAl-AR (14 h under reaction at  $T = 500\text{--}800\text{ }^{\circ}\text{C}$ ) and 4NiAl-ST (120 h under reaction at 700 °C). (e) OM images of 4NiAl-ST.

with the conversion value decreasing *ca.* 11%, from 85% to 74%. As the drop in CO<sub>2</sub> conversion was a bit less than that in CH<sub>4</sub> conversion, the syngas ratio slightly decreased from 0.97 at 1 h to 0.92 at 120 h (Fig. 2e). This suggests that coke formation deactivated some active sites, without significantly triggering secondary reactions like the reverse water–gas shift (RWGS) or CH<sub>4</sub> decomposition.

Post-reaction characterization included TGA analysis of used NiAl samples after 14 h of screening tests (500–800 °C) in air, showing weight loss from coke oxidation (Fig. 3c). The 4NiAl sample after the 120 h stability test at 700 °C (4NiAl-ST) exhibited lower weight loss than 16NiAl, despite the latter undergoing only 14 h of reaction (Fig. 3c). This highlights the importance of optimizing catalyst composition to enhance long-term performance, while minimizing deactivation and solid carbon (*i.e.*, coke/soot) accumulation, which could cause increased reactor pressure drops.

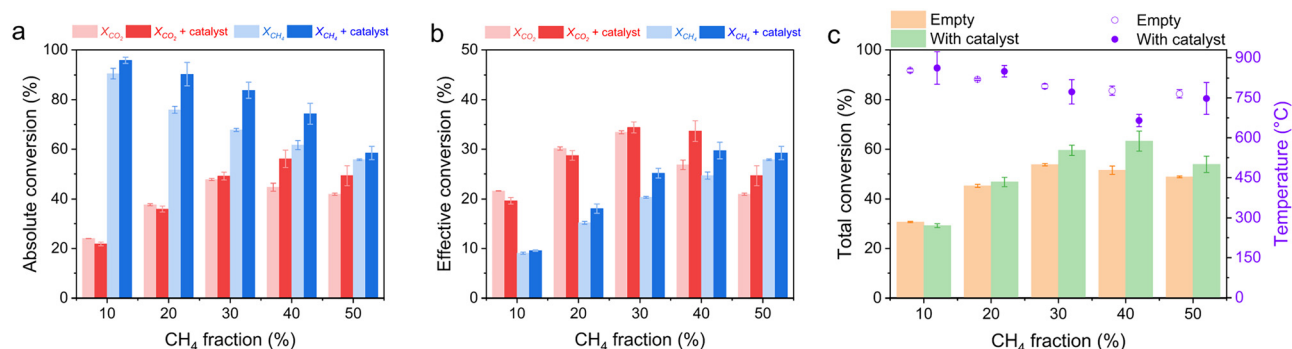
XPS analysis of 4NiAl after the stability test (4NiAl-ST) revealed Ni 2p<sub>3/2</sub> peaks corresponding to Ni<sup>2+</sup> (NiO) and metallic Ni (Fig. 3a and b). The Ni<sup>0</sup> peak in 4NiAl-ST was shifted to a lower binding energy (BE) compared to 4NiAl-act, suggesting weaker Ni-support interactions (Fig. 3a), and the formation of larger Ni nanoparticles. XRD analysis confirmed this, showing Ni<sup>0</sup> nanoparticle sintering in used 4NiAl samples (4NiAl-AR (*i.e.*, after reaction of 14 h): 15 nm and 4NiAl-ST: 18 nm), with no crystalline NiO detected (Fig. 3d).

The C 1s XPS spectrum of 4NiAl-ST showed a high-intensity peak at 283.0 eV and 283.4 eV, indicating different types of coke (Fig. 3b).<sup>39</sup> Additionally, a lower BE feature suggests carbide carbon (Ni–C).<sup>39,42,43</sup> XRD patterns of 4NiAl-ST supported the formation of solid carbon (coke), showing a broad peak at  $2\theta = 26^{\circ}$  (Fig. 3d). The presence of solid carbon was also visually evident from the coloration of the sample after the reaction (Fig. 3e). Solid carbon deposition reduced the  $S_{\text{BET}}$  surface area and pore volume of 4NiAl after the stability test, with values decreasing from 156 to 116 m<sup>2</sup> g<sup>−1</sup> for  $S_{\text{BET}}$  and 0.45 to 0.32 cm<sup>3</sup> g<sup>−1</sup> for  $V_p$ , respectively (Fig. S8, ESI<sup>†</sup>). Hg intrusion porosimetry of 4NiAl-ST further confirmed pore blockage, as indicated by a decrease in total pore volume (Fig. S5, ESI<sup>†</sup>).

### 3.3. Plasma-catalytic DRM tests

**3.3.1. Conversion.** To boost both the conversion and production rates of plasma-based DRM, a Ni catalyst (4NiAl) with the demonstrated thermo-catalytic activity was implemented downstream from the plasma reactor. The absolute conversion of CO<sub>2</sub> and CH<sub>4</sub> as a function of CH<sub>4</sub> fraction at the inlet are shown in Fig. 4a, both in the absence and presence of said catalyst.

At low CH<sub>4</sub> fractions (*i.e.* 10 and 20 vol%), the presence of a catalyst has a small negative effect on the CO<sub>2</sub> conversion, *i.e.*, *ca.* 2% reduction in conversion. This reduction is likely due to



**Fig. 4** Performance of the post-plasma-catalytic DRM reaction using 4NiAl-act sample. (a) Absolute conversion of CO<sub>2</sub> and CH<sub>4</sub> with and without catalyst, (b) effective conversion of CO<sub>2</sub> and CH<sub>4</sub> with and without catalyst, and (c) total conversion of CO<sub>2</sub> and CH<sub>4</sub> with and without catalyst. The 4NiAl sample was *ex situ* activated (H<sub>2</sub>/N<sub>2</sub> = 1/1,  $T = 750\text{ }^{\circ}\text{C}$ ) prior to testing.



an enhanced water gas shift (WGS) reaction, in which CO and H<sub>2</sub>O react to form CO<sub>2</sub> and H<sub>2</sub>. The forward reaction proceeds instead of the reverse (RWGS) reaction due to insufficient H<sub>2</sub>. As the CH<sub>4</sub> fraction increases, the proportion of H<sub>2</sub>O formed decreases. As this occurs, the rate of the WGS reaction also decreases, resulting in a small rise in CO<sub>2</sub> conversion at 30 vol% CH<sub>4</sub> inlet fraction (+2%). At the highest examined CH<sub>4</sub> fractions (40 and 50 vol%), solid carbon deposition from the CH<sub>4</sub> decomposition becomes more prevalent. While this is detrimental for the catalyst activity and leads to deactivation, the produced solid carbon can react with the gas phase CO<sub>2</sub> via the reverse Boudouard reaction to increase the CO<sub>2</sub> conversion.<sup>31,44,45</sup> As a result, the optimum CO<sub>2</sub> conversion in the presence of a catalyst is achieved with 40 vol% CH<sub>4</sub> at the inlet (+10% rise compared to without catalyst).

For the CH<sub>4</sub> conversion, the presence of the catalyst improves the performance for all examined CH<sub>4</sub> fractions. Upon increasing CH<sub>4</sub> fraction at the inlet, the absolute conversion decreases from a maximum value around 96% (10 vol% CH<sub>4</sub>, with catalyst) to 59% (50 vol% CH<sub>4</sub>, with catalyst). The largest proportional increase upon adding the catalyst is observed with 30 vol% CH<sub>4</sub> fraction at the inlet, with the conversion increasing by approximately 24% (from 68% to 84%). The lower effectiveness of the catalyst at higher CH<sub>4</sub> fractions (40 and 50 vol%) is likely due to coke deposition and the resulting catalyst deactivation, as also observed in the thermal DRM (Fig. 2 and 3).

Direct comparison to the conversions obtained by thermal-catalytic testing is not possible due to the presence of a diluting gas in the thermal cases (N<sub>2</sub>), which was needed to limit solid carbon production and thus enable longer experiments. However, we can contrast the absolute conversions realised with 50 vol% CH<sub>4</sub> in the PPC case to those obtained in the thermal-catalytic tests for 4NiAl around 700 °C (Fig. 4a and b). Interestingly, the CO<sub>2</sub> conversion is lower while the CH<sub>4</sub> conversion is higher in the PPC scenario. This difference likely arises due to the fact that conversion occurs in the plasma reactor prior to entering the bed, as shown in the empty bed case (Fig. 4a). This pre-bed conversion effect coupled with the dilution required in the thermal-catalytic experiments serves to highlight the fact that direct comparison between the thermal and PPC experiments is not applicable, and that the results obtained in the thermal-catalytic case are simply indicators of a potential coupling. Replicating the plasma effluent mixture obtained from pre-bed reactant conversions and their effect on the thermal-catalytic conversion would be an interesting avenue of study, but is outside the scope of this work.

While high absolute reactant conversions can be obtained, especially highlighted by the near complete CH<sub>4</sub> conversion with catalyst at 10 vol% CH<sub>4</sub> (Fig. 4a), the effective conversion is a more relevant metric to account for the proportion of inlet stream that contains the reactant of interest (eqn (S8), ESI†). Thus, the effective conversion of CO<sub>2</sub> and CH<sub>4</sub> in the presence and absence of catalyst as a function of CH<sub>4</sub> inlet fraction is shown in Fig. 4b. At a single inlet fraction, the absence or presence of a catalyst follows the same trend as the absolute

conversion for both CO<sub>2</sub> and CH<sub>4</sub>. The effective CO<sub>2</sub> conversion peaks around 30 to 40 vol%, reaching a maximum value around 34%. Contrary to the absolute CH<sub>4</sub> conversion trend, the effective conversion increases as a function of increasing CH<sub>4</sub> inlet fraction, peaking around 30% for the inlet fractions of 40 and 50 vol%.

The absolute conversion values achieved in this work are lower than those reported by Xu *et al.*,<sup>29</sup> especially when compared at the same molar ratio of CO<sub>2</sub>/CH<sub>4</sub> (*i.e.* 1/1 or 50 vol% CH<sub>4</sub>). However, we used a non-dilute CO<sub>2</sub>/CH<sub>4</sub> stream as the feed gas, whereas Xu *et al.*<sup>29</sup> utilised an inlet stream of only 10 vol% CO<sub>2</sub> and 10 vol% CH<sub>4</sub>, heavily diluted with N<sub>2</sub> (80 vol%).

The authors did so to facilitate plasma ignition and sustainment at this ratio, while minimizing coke deposition, and it was reported several times that N<sub>2</sub> enhances the (absolute) CO<sub>2</sub> and CH<sub>4</sub> conversion.<sup>46–49</sup> Hence, we advocate that the effective conversion is a more comparable metric, as it accounts for the proportion of reactant converted with regards to the amount supplied at the inlet. The corresponding best effective CO<sub>2</sub> and CH<sub>4</sub> conversion values achieved by Xu *et al.* were 7 and 9%, respectively (Table 2). When compared to the effective conversion obtained with our setup (Fig. 4b), all examined conditions in our study demonstrate an improvement. The highest effective CO<sub>2</sub> conversion is achieved at both 30 and 40 vol% CH<sub>4</sub> at the inlet, reaching a value around 34%. The peak effective CH<sub>4</sub> conversion is achieved at 40 vol% CH<sub>4</sub>, reaching 30%. The five-fold increase in effective CO<sub>2</sub> conversion and three-fold increase in effective CH<sub>4</sub> conversion demonstrate the detrimental effect of dilution on the performance. In addition to reducing the effective conversion values, the cost and complexity of separating the effluent mixture also increases with dilution, making the process less appealing for scaled-up applications, and therefore for cost-effective industrial processes.

Other than effective conversion, the total conversion can also be used to provide a more global view of the process performance.<sup>36</sup> As this is a summation of the effective conversion values (eqn (S9), ESI†), the effect of dilution is also considered. Xu *et al.* obtained a peak total conversion of *ca.* 16%,<sup>28</sup> whereas we obtained values up to 63% (at 40 vol% CH<sub>4</sub> inlet fraction), which is nearly four times higher (Fig. 4c). In addition, the temperature measured inside the post-plasma catalyst bed (T1) is shown in Fig. 4c, with all four thermocouple readings shown in Fig. 5 (T1–T4, see setup schematic in Fig. S1b, ESI†). For both empty and filled cases, the increasing CH<sub>4</sub> fraction in the inlet feed resulted in a lower temperature in the bed and reactor exhaust. This correlates with previous observations in literature<sup>33,50</sup> and is associated with the changes to the mixture thermal conductivity and heat capacity.<sup>50</sup> As demonstrated by the CO<sub>2</sub> and CH<sub>4</sub> conversion shown in the thermal catalytic tests (Fig. 2a and b), the optimum catalyst temperature is around 800 °C. In the PPC cases, 10% CH<sub>4</sub> at the inlet slightly overshoots this ideal temperature, reaching bed temperatures around 900 °C, while 30–50% CH<sub>4</sub> inlet concentrations slightly undershoot the optimum temperature (bed temperature *ca.* 700 °C). Only with 20



Table 2 Overview of post-plasma-catalytic DRM literature

| Reactor type           | Catalyst                                            | Diluting gas       | CO <sub>2</sub> :CH <sub>4</sub> | Total flow (L min <sup>-1</sup> ) | Power (kW) | Absolute conversion (%) |                 | Effective conversion (%) |                 | (MJ mol <sup>-1</sup> reactants) | Ref.      |
|------------------------|-----------------------------------------------------|--------------------|----------------------------------|-----------------------------------|------------|-------------------------|-----------------|--------------------------|-----------------|----------------------------------|-----------|
|                        |                                                     |                    |                                  |                                   |            | CO <sub>2</sub>         | CH <sub>4</sub> | CO <sub>2</sub>          | CH <sub>4</sub> |                                  |           |
| Glow discharge         | —                                                   | —                  | 3:1                              | 1                                 | —          | 55                      | 85              | 41                       | 21              | 0.34                             | 51        |
| Rotating gliding arc   | —                                                   | 70% Ar             | 1:1                              | 3.7                               | 0.16       | 10.9                    | 12.8            | 1.6                      | 1.9             | 4.6                              | 52        |
| Microwave              | —                                                   | —                  | 1:1                              | 30                                | 6          | 70                      | 96              | 35                       | 48              | 0.35                             | 53        |
| Thermal arc            | Ni/Al <sub>2</sub> O <sub>3</sub>                   | 77% N <sub>2</sub> | 3:2                              | 36.7                              | 9.6        | 88                      | 76              | 10.5                     | 7               | 89.8                             | 23        |
| Thermal arc            | Ni/Al <sub>2</sub> O <sub>3</sub>                   | 16% Ar             | 3:2                              | 117                               | 14.4       | 77                      | 62.4            | 29.2                     | 15.8            | 16.4                             | 24        |
|                        |                                                     | 27% N <sub>2</sub> |                                  |                                   |            |                         |                 |                          |                 |                                  |           |
| Planar gliding arc     | NiO/Al <sub>2</sub> O <sub>3</sub>                  | —                  | 1:1                              | 2.5                               | 0.15       | 19                      | 17              | 9.5                      | 8.5             | 20                               | 25        |
| Rotating gliding arc   | Ni/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | —                  | 7:3                              | 6                                 | 0.49       | 39.5                    | 58.5            | 11.9                     | 41              | 9.3                              | 26        |
| Rotating gliding arc   | Ni/Al <sub>2</sub> O <sub>3</sub>                   | —                  | 1:1                              | 2.7                               | 0.49       | 91                      | 94              | 45.5                     | 47              | 12                               | 27        |
| Rotating gliding arc   | Ni/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | 70% Ar             | 3:2                              | 3.7                               | 0.14       | 10.9                    | 11.8            | 2                        | 1.4             | 65.3                             | 28        |
| Gliding arc plasmatron | Ni/LDH                                              | 80% N <sub>2</sub> | 1:1                              | 8                                 | 0.51       | 79                      | 91              | 7.9                      | 9.1             | 0.52                             | 29        |
| Gliding arc plasmatron | Ni/Al <sub>2</sub> O <sub>3</sub>                   | —                  | 3:2                              | 10                                | 1.05       | 56                      | 74              | 33                       | 29              | 0.24                             | This work |

vol% CH<sub>4</sub> prescribed at the inlet reaches the ideal bed temperature (*ca.* 800 °C) at the applied current. The conversion realised at 10 vol% CH<sub>4</sub> and 30–50 vol% CH<sub>4</sub> could be improved by either reducing or increasing the catalyst bed temperature respectively, which is achieved by decreasing or elevating the SEI at these conditions. This can be achieved either by power or flow rate regulation, with the former being achieved by current modulation. Nevertheless, in general, all conditions yield catalyst bed temperatures in the range of optimal performance determined by the thermal-catalytic testing. For all examined cases, the temperature decreases as the gas travels through the plasma reactor exhaust (*i.e.*, from T2 to T4). This occurs due to the conductive heat losses through the stainless steel exhaust walls.

**3.3.2. Production rates and syngas ratio.** The production rates of both CO and H<sub>2</sub> per mole of Ni loading as a function of CH<sub>4</sub> fraction supplied at the inlet are shown in Fig. 6a.

When rising the inlet fraction from 10 to 40 vol% CH<sub>4</sub>, both CO and H<sub>2</sub> production rates increase. The CO rate increases from 10.7 molCO mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup> at 10 vol% CH<sub>4</sub> to a peak value of *ca.* 24.3 molCO mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup> at 40 vol% CH<sub>4</sub>. Concurrently, the H<sub>2</sub> production rate increases from 4.1 molH<sub>2</sub> mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup> to a near-equal peak value of 24.4 molH<sub>2</sub> mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup> at the same data points. Interestingly, at 50 vol% CH<sub>4</sub>, the molar CO production rate decreases to *ca.* 19.6 molCO mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup>. This drop can be attributed to the lower CO<sub>2</sub> concentration in the inlet, which acts as the limiting reactant for CO production.

At the same inlet CH<sub>4</sub> fraction, the H<sub>2</sub> production rate remains relatively constant (*ca.* 24.5 molH<sub>2</sub> mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup>) despite a drop in absolute conversion. This is due to the CH<sub>4</sub> decomposition, which remains constant at this CH<sub>4</sub> concentration. This levelling occurs as the drop in volumetric flow rate at the exhaust (observed with increasing fraction of CH<sub>4</sub> at the inlet due to solid carbon formation) is proportional to the drop in the outlet CO concentration (see eqn (S10), ESI†).

In comparison to the production rates realised in the thermo-catalytic tests (Fig. 2c and d), both CO and H<sub>2</sub> production rates are significantly increased in our post-plasma catalysis experiments. These trends are logical, as the GHSV increases by an order of magnitude between the experimental setups. The CO production rate is enhanced almost five-fold for the lowest plasma-based case (from 2.4 to 10.7 molCO mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup>), a value which is more than doubled to 24.3 molCO mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup> at the highest CO production rate (at 40 vol% CH<sub>4</sub> inlet fraction), leading to ten times higher CO production rate in post-plasma catalysis *vs.* thermal catalysis. The H<sub>2</sub> production rate is similarly enhanced. Although the enhancement is less than two-fold in the lowest case (10% CH<sub>4</sub> inlet fraction) from 2.5 to 4.1 molH<sub>2</sub> mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup>, it elevates rapidly with increasing inlet CH<sub>4</sub> fraction, resulting in a peak value increasing again ten-fold when compared to the best result in thermal catalysis (from 2.5 to 24.5 molH<sub>2</sub> mol<sub>Ni</sub><sup>-1</sup> min<sup>-1</sup>). The dramatic increase in production rates in the PPC experiments

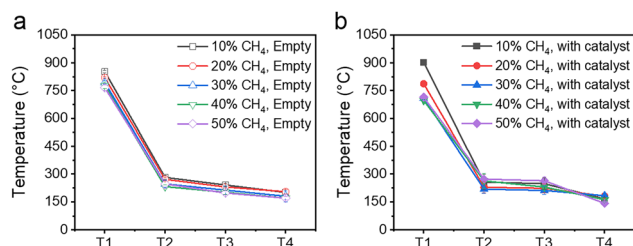


Fig. 5 Average temperature with (a) empty catalyst and (b) filled catalyst bed with 4NiAl. Recorded at four locations along reactor body (T1 = inside catalyst bed, T2 = 10 cm from reactor outlet, T3 = 20 cm from reactor outlet, T4 = 30 cm from reactor outlet).

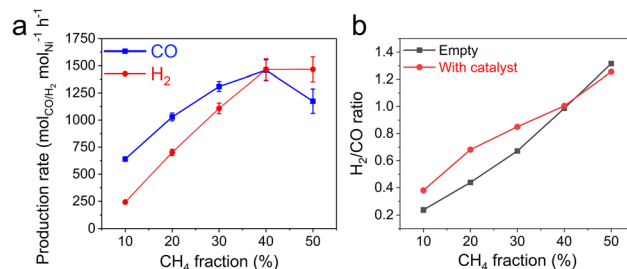


Fig. 6 Performance of the post-plasma-catalytic DRM reaction using 4NiAl-act sample. (a) Molar production rate of CO and H<sub>2</sub> in relation to Ni loading, and (b) syngas ratio (H<sub>2</sub>/CO) as a function of increasing CH<sub>4</sub> inlet concentration. The 4NiAl sample was *ex situ* activated (H<sub>2</sub>/N<sub>2</sub> = 1/1, T = 750 °C) prior to testing.





can be attributed to the high absolute conversion of  $\text{CO}_2$  and  $\text{CH}_4$  in combination with the higher flow rates (and hence increased GHSV) in the plasma reactor setup. These improvements serve to highlight the potential advantage of implementing an optimised thermal catalyst downstream from a plasma reactor, enhancing both conversion and syngas production rates compared to operating plasma without a catalyst. Indeed, scaling up of the process from a smaller-scale thermal catalysis setup to a larger-scale plasma system is demonstrated by the increased production rates of  $\text{CO}$  and  $\text{H}_2$ .

The syngas ratio ( $\text{H}_2/\text{CO}$ ) (Fig. 6b) increases with  $\text{CH}_4$  fraction, both in the presence and absence of the catalyst. The increased amount of  $\text{CH}_4$  at the inlet produces more  $\text{H}_2$ , which rises faster than the  $\text{CO}$  production rate (Fig. 6a), explaining the logical trend in Fig. 6b. Additionally, when the catalyst is incorporated downstream, we observe a slightly higher syngas ratio (1.25–1.5 fold) compared to the empty plasma reactor in the range of 10 to 30 vol%  $\text{CH}_4$ . At 40 vol%, the catalyst presence has no significant effect on the ratio, whereas for 50 vol% we observe a slightly detrimental effect. The explanation for this is two-fold, firstly by the greater carbon deposition from the improved dehydrogenation capability of the Ni catalyst, which promotes  $\text{CH}_4$  decomposition. This solid carbon can then be oxidised by the  $\text{CO}_2$  via the reverse Boudouard reaction, which increases the  $\text{CO}$  production. Secondly, the conversion of  $\text{CH}_4$  is lower at 50 vol%  $\text{CH}_4$ , and both factors contribute to a lower syngas ratio in the presence of catalyst at this fraction.

**3.3.3. Energy cost.** The EC realised with our setup for all inlet  $\text{CH}_4$  fractions is shown in Fig. 7. The EC remains relatively constant between the empty bed and the bed with the packed catalyst for all inlet  $\text{CH}_4$  fractions. We observe the lowest EC at 40 vol%  $\text{CH}_4$  at the inlet, reaching around  $0.24 \text{ MJ mol}^{-1}$  (with or without catalyst). At 50 vol%  $\text{CH}_4$  inlet fraction, the EC is slightly higher, reaching  $0.28 \text{ MJ mol}^{-1}$ , both with and without

catalyst present. This can be correlated to the lower total conversion observed at this data point (Fig. 4c).

When comparing these results with the EC values obtained by Xu *et al.*,<sup>29</sup> who used a similar reactor setup and catalyst (*i.e.* GAP and Ni-based), we should note that Xu *et al.* reported the EC related exclusively to the effective conversion of  $\text{CO}_2$ . While this formula can be applied if the focus is on  $\text{CO}_2$  conversion, the DRM-oriented research best uses the EC values calculated based on the recommendation of Wanten *et al.*,<sup>36</sup> *i.e.* on the total conversion (eqn (S9), ESI†). As such, the effective conversion of both  $\text{CO}_2$  and  $\text{CH}_4$  is considered. If the same equation is applied to the results of Xu *et al.*, the authors reached an optimum EC of  $0.52 \text{ MJ mol}^{-1}$ . Thus, our EC is about a factor two lower for all examined  $\text{CH}_4$  inlet fractions, especially at the optimum inlet fractions of 30 and 40 vol%  $\text{CH}_4$  ( $\text{EC} = 0.25 \text{ MJ mol}^{-1}$ ).

Finally, we also compared our results with other data reported in literature for post-plasma-catalytic DRM with various plasma reactors, shown in Table 2. Evidently, several different types of reactors have been investigated, with most implementing a thermal plasma. This is logical, as PPC utilises sensible or waste heat from the plasma reactor to facilitate the catalysis.

For the sake of completeness, we also added a few entries of plasma-based DRM without catalysts. While they are often characterised by lower conversion and higher EC, the examples shown are some of the best results in literature to-date. Nonetheless, the realised ECs are slightly worse than those obtained in this study. However, the latter comes with the cost of adding a catalyst. Overall, a main advantage of post-plasma catalysis is the utilisation of the waste heat from the plasma reactor to heat the catalyst bed, which equates to heat integration. Heat integration could in principle also be performed without catalyst, by using the effluent heat to preheat the inlet gas (so that less power is needed to reach the same level of conversion), but this is not yet commonplace in plasma reactors.

It is clear that the EC realised at the optimum condition in our study is the lowest reported in literature to date, with mostly higher effective  $\text{CO}_2$  and  $\text{CH}_4$  conversions.

**3.3.4. Extended catalytic test.** To further establish the viability of post-plasma-catalytic DRM, we conducted a long-run test of 6 h for 30 vol%  $\text{CH}_4$  at the inlet, which is shown in Fig. 8. While an inlet  $\text{CH}_4$  fraction of 30 vol% did not produce the highest conversion or the lowest EC (see above), this condition yielded significantly less carbon deposition than 40 or 50 vol%  $\text{CH}_4$ , while also demonstrating the greatest EC improvement when comparing the results with and without catalyst. Hence, this fraction was deemed the most viable for a long-run test.

As seen in Fig. 8, the  $\text{CO}_2$  and  $\text{CH}_4$  fractions decrease rapidly upon plasma ignition, with the  $\text{CO}_2$  decreasing from 70 to *ca.* 25 vol% after 10 min, and  $\text{CH}_4$  decreasing from 30 to 4 vol% in the same period. These values continue to decline until about 60 min, after which they remain constant around 22 vol% and 2.5 vol%, respectively, for the remainder of the test. Simultaneously, the  $\text{CO}$  and  $\text{H}_2$  values increase dramatically in the first 10 min, reaching values around 39 and 32 vol%, respectively. These values rise further until about 60 min, reaching again

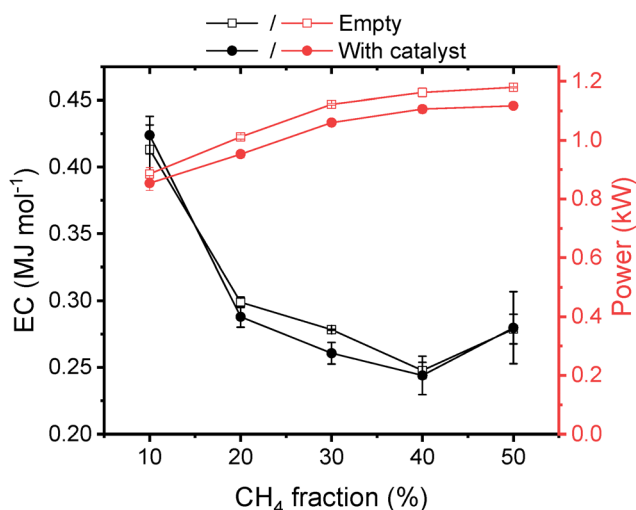


Fig. 7 Performance of the post-plasma-catalytic DRM reaction using 4NiAl-act sample. Energy cost (per mol of reactant mixture) for total conversion as a function of increasing inlet  $\text{CH}_4$  fraction. The 4NiAl sample was *ex situ* activated ( $\text{H}_2/\text{N}_2 = 1/1$ ,  $T = 750^\circ\text{C}$ ) prior to testing.



## Notes and references

- 1 K. Wittich, M. Krämer, N. Bottke and S. A. Schunk, *Chem-CatChem*, 2020, **12**, 2130–2147.
- 2 H. Zhu, H. Chen, M. Zhang, C. Liang and L. Duan, *Catal. Sci. Technol.*, 2024, **14**, 1712–1729.
- 3 R. K. Parsapur, S. Chatterjee and K. W. Huang, *ACS Energy Lett.*, 2020, **5**, 2881–2885.
- 4 M. Lu, X. Zhang, J. Deng, S. Kuboon, K. Faungnawakij, S. Xiao and D. Zhang, *Catal. Sci. Technol.*, 2020, **10**, 4237–4244.
- 5 J. M. Ginsburg, J. Piña, T. El Solh and H. I. De Lasa, *Ind. Eng. Chem. Res.*, 2005, **44**, 4846–4854.
- 6 J. Yu, T. Le, D. Jing, E. Stavitski, N. Hunter, K. Lalit, D. Leshchev, D. E. Resasco, E. H. Sargent, B. Wang and W. Huang, *Nat. Commun.*, 2023, **14**, 1–9.
- 7 L. Wu, X. Xie, H. Ren and X. Gao, *Mater. Today: Proc.*, 2021, **42**, 153–160.
- 8 X. Liu, L. Zhang, X. Zheng, Y. Zhang, D. He and Y. Luo, *Int. J. Hydrogen Energy*, 2022, **47**, 30937–30949.
- 9 M. Trueba and S. P. Trasatti, *Eur. J. Inorg. Chem.*, 2005, 3393–3403.
- 10 R. Snoeckx and A. Bogaerts, *Chem. Soc. Rev.*, 2017, **46**, 5805–5863.
- 11 A. Bogaerts and E. C. Neyts, *ACS Energy Lett.*, 2018, **3**, 1013–1027.
- 12 H. Hosseini, *RSC Adv.*, 2023, **13**, 28211–28223.
- 13 K. Li, S. Chen, H. Guo, M. Li, L. Zhong, Q. Sun and F. Wang, *IEEE Trans. Plasma Sci.*, 2024, **52**, 2180–2187.
- 14 Y. Gorbanev, I. Fedirchuk and A. Bogaerts, *Curr. Opin. Green Sustainable Chem.*, 2024, **47**, 100916.
- 15 R. De Meyer, Y. Gorbanev, R. G. Ciocarlan, P. Cool, S. Bals and A. Bogaerts, *Chem. Eng. J.*, 2024, **488**, 150838.
- 16 C. Ndayirinde, Y. Gorbanev, R. G. Ciocarlan, R. De Meyer, A. Smets, E. Vlasov, S. Bals, P. Cool and A. Bogaerts, *Catal. Today*, 2023, **419**, 114156.
- 17 S. W. Brown, S. Tiwari and J. Hu, *Plasma Processes Polym.*, 2024, **21**, e2400050.
- 18 S. Tiwari, S. A. Ibrahim, B. Robinson, S. Brown, Q. Wang, F. Che and J. Hu, *Catal. Sci. Technol.*, 2023, **13**, 2966–2981.
- 19 G. Chen, V. Georgieva, T. Godfroid, R. Snyders and M. P. Delplancke-Ogletree, *Appl. Catal., B*, 2016, **190**, 115–124.
- 20 M. Młotek, J. Sentek, K. Krawczyk and K. Schmidt-Szałowski, *Appl. Catal., A*, 2009, **366**, 232–241.
- 21 K. Li, J. L. Liu, X. S. Li, X. Zhu and A. M. Zhu, *Chem. Eng. J.*, 2016, **288**, 671–679.
- 22 Q. F. Lin, Y. M. Jiang, C. Z. Liu, L. W. Chen, W. J. Zhang, J. Ding and J. G. Li, *Energy Rep.*, 2021, **7**, 4064–4070.
- 23 X. Tao, F. Qi, Y. Yin and X. Dai, *Int. J. Hydrogen Energy*, 2008, **33**, 1262–1265.
- 24 Y. Xu, Q. Wei, H. Long, X. Zhang, S. Shang, X. Dai and Y. Yin, *Int. J. Hydrogen Energy*, 2013, **38**, 1384–1390.
- 25 Z. A. Allah and J. C. Whitehead, *Catal. Today*, 2015, **256**, 76–79.
- 26 F. Zhu, H. Zhang, X. Yan, J. Yan, M. Ni, X. Li and X. Tu, *Fuel*, 2017, **199**, 430–437.
- 27 J. L. Liu, Z. Li, J. H. Liu, K. Li, H. Y. Lian, X. S. Li, X. Zhu and A. M. Zhu, *Catal. Today*, 2019, **330**, 54–60.
- 28 J. Martin-Del-Campo, M. Uceda, S. Coulombe and J. Kopyscinski, *J. CO<sub>2</sub> Util.*, 2021, **46**, 101474.
- 29 W. Xu, L. C. Buelens, V. V. Galvita, A. Bogaerts and V. Meynen, *J. CO<sub>2</sub> Util.*, 2024, **83**, 102820.
- 30 B. Wanten, Y. Gorbanev and A. Bogaerts, *Fuel*, 2024, **374**, 132355.
- 31 C. O'Modhrain, Y. Gorbanev and A. Bogaerts, *J. Energy Chem.*, 2025, **104**, 312–323.
- 32 T. Nunnally, K. Gutsol, A. Rabinovich, A. Fridman, A. Gutsol and A. Kemoun, *J. Phys. D: Appl. Phys.*, 2011, **44**, 274009.
- 33 E. Cleiren, S. Heijckers, M. Ramakers and A. Bogaerts, *ChemSusChem*, 2017, **10**, 4025–4036.
- 34 S. A. Wutzke, E. Pfender and E. R. G. Eckert, *AIAA J.*, 1967, **5**, 707–713.
- 35 I. Tsonev, C. O'Modhrain, A. Bogaerts and Y. Gorbanev, *ACS Sustainable Chem. Eng.*, 2023, **11**, 1888–1897.
- 36 B. Wanten, R. Vertongen, R. De Meyer and A. Bogaerts, *J. Energy Chem.*, 2023, **86**, 180–196.
- 37 Y. Kwon, J. E. Eichler and C. B. Mullins, *J. CO<sub>2</sub> Util.*, 2022, **63**, 102112.
- 38 M. A. Goula, N. D. Charisiou, K. N. Papageridis, A. Delimitis, E. Pachatouridou and E. F. Iliopoulou, *Int. J. Hydrogen Energy*, 2015, **40**, 9183–9200.
- 39 J. Guo, H. Lou, H. Zhao, D. Chai and X. Zheng, *Appl. Catal., A*, 2004, **273**, 75–82.
- 40 N. F. P. Ribeiro, R. C. R. Neto, S. F. Moya, M. M. V. M. Souza and M. Schmal, *Int. J. Hydrogen Energy*, 2010, **35**, 11725.
- 41 R. Wang, Y. Li, R. Shi and M. Yang, *J. Mol. Catal. A: Chem.*, 2011, **344**, 122–127.
- 42 A. M. Venezia, R. Bertoncello and G. Deganello, *Surf. Interface Anal.*, 1995, **23**, 239–247.
- 43 L. Sandoval-Diaz, D. Cruz, M. Vuijk, G. Ducci, M. Hävecker, W. Jiang, M. Plodinec, A. Hammud, D. Ivanov, T. Götsch, K. Reuter, R. Schlögl, C. Scheurer, A. Knop-Gericke and T. Lunkenbein, *Nat. Catal.*, 2024, **7**, 161–171.
- 44 M. Hasegawa, K. Sugawara, R. Suto, S. Sambonsuge, Y. Teraoka, A. Yoshigoe, S. Filimonov, H. Fukidome and M. Suemitsu, *Nanoscale Res. Lett.*, 2015, **10**, 1–6.
- 45 O. Biondo, K. Wang, H. Zhang and A. Bogaerts, *Chem. Eng. J.*, 2025, **507**, 160190.
- 46 R. Snoeckx, S. Heijckers, K. Van Wesenbeeck, S. Lenaerts and A. Bogaerts, *Energy Environ. Sci.*, 2016, **9**, 999–1011.
- 47 M. Ramakers, S. Heijckers, T. Tytgat, S. Lenaerts and A. Bogaerts, *J. CO<sub>2</sub> Util.*, 2019, **33**, 121–130.
- 48 J. Slaets, M. Aghaei, S. Ceulemans, S. Van Alphen and A. Bogaerts, *Green Chem.*, 2020, **22**, 1366–1377.
- 49 W. Xu, S. Van Alphen, V. V. Galvita, V. Meynen and A. Bogaerts, *ChemSusChem*, 2024, **17**, e202400169.
- 50 J. Slaets, E. Morais and A. Bogaerts, *RSC Sustainability*, 2025, **3**, 1477–1493.
- 51 B. Wanten, S. Maerivoet, C. Vantomme, J. Slaets, G. Trenchev and A. Bogaerts, *J. CO<sub>2</sub> Util.*, 2022, **56**, 101869.
- 52 J. Martin-del-Campo, S. Coulombe and J. Kopyscinski, *Plasma Chem. Plasma Process.*, 2020, **40**, 857–881.
- 53 S. M. Chun, Y. C. Hong and D. H. Choi, *J. CO<sub>2</sub> Util.*, 2017, **19**, 221–229.

