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## Selective catalytic hydrogenation of C<sub>2</sub>H<sub>2</sub> from plasma-driven CH<sub>4</sub> coupling without extra heat: mechanistic insights from micro-kinetic modelling and reactor performance†

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We study the selective catalytic hydrogenation of C<sub>2</sub>H<sub>2</sub>, the main product from non-oxidative CH<sub>4</sub> coupling in gas-phase plasmas, to C<sub>2</sub>H<sub>4</sub>, a cornerstone of the global chemical industry, by experiments and temperature-dependent micro-kinetic modelling. The model is validated against new experimental data from a nanosecond pulsed plasma reactor integrated with a downstream catalytic bed consisting of Pd/Al<sub>2</sub>O<sub>3</sub>. We explore the effects of varying Pd loadings (0.1, 0.5, and 1 wt%) on the catalyst activity and the C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> product distribution. Consistent with the experimental data, our surface micro-kinetic model shows that while higher Pd loadings lower the catalyst activation temperature for C<sub>2</sub>H<sub>2</sub> conversion, they also induce over-hydrogenation to C<sub>2</sub>H<sub>6</sub> at lower temperatures and increase oligomerisation in the experiments, which are detrimental to the C<sub>2</sub>H<sub>4</sub> yield. The model also elucidates reaction mechanisms and pathways across different temperature regimes, expanding our understanding of the hydrogenation process beyond the experimental range. Besides highlighting the importance of optimising the metal loading to balance C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> selectivity, our findings demonstrate the effective implementation of post-plasma catalysis using a simple catalyst bed heated by hot gas from the plasma region. This study opens possibilities for testing different plasma sources, catalysts, gas flow magnitude and patterns, and catalyst bed-to-plasma distances.

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### Broader context

The direct conversion of methane (CH<sub>4</sub>) to ethylene (C<sub>2</sub>H<sub>4</sub>) is thermodynamically challenging yet critical, given the demand for sustainable methods to synthesise valuable base chemicals, such as ethylene – a core molecule in global industry. The integration of plasma reactors with catalysis offers a promising solution, as it provides an efficient tool for CH<sub>4</sub> coupling into C<sub>2</sub>H<sub>2</sub>, followed by a pathway to selectively steer the reaction towards C<sub>2</sub>H<sub>4</sub>. In this study, we demonstrate this synergy by catalytically hydrogenating the C<sub>2</sub>H<sub>2</sub> plasma-product into C<sub>2</sub>H<sub>4</sub> using Pd catalysts activated by the hot gas stream exiting the plasma reactor, without external heating. Alongside, we developed a temperature-dependent micro-kinetic surface model, providing insights into optimising C<sub>2</sub>H<sub>4</sub> selectivity and avoiding C<sub>2</sub>H<sub>6</sub> and oligomerisation by-products by balancing catalyst metal loading and reaction temperature. Our results broaden the understanding of coupling plasma to downstream catalysis and open new avenues for developing electrified, scalable and energy-efficient processes for ethylene synthesis and methane valorisation. These findings highlight the potential of plasma and post-plasma catalysis to play a central role in fostering a CO<sub>2</sub>-neutral chemical industry and promoting a more sustainable future, as well as providing a framework for further research into energy and environmental (plasma) catalysis.

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## 1. Introduction

The emergence of plasma technologies for converting predominantly inert gases (such as CO<sub>2</sub> and CH<sub>4</sub>) marks an important development within the efforts to shift the chemical synthesis of highly valuable light molecules, like C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>OH, from naphtha cracking to electrified processes with a neutral CO<sub>2</sub> loop.<sup>1,2</sup> The transition from traditional routes to plasma-based synthesis has positive techno-economic and



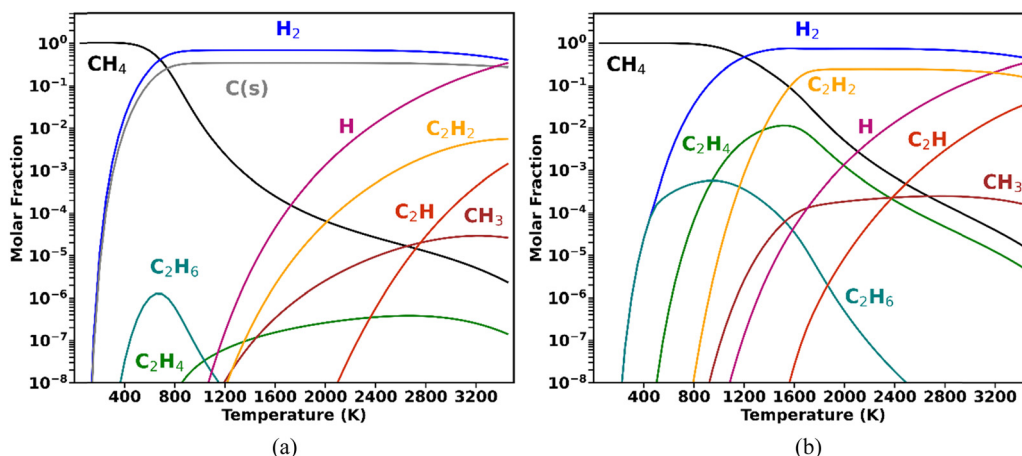


Fig. 1 Gas-phase equilibrium composition at 1 bar, initiated with 1 mole of  $\text{CH}_4$ , under two assumptions: (a) solid carbon is formed in equilibrium with the gas phase, or (b) there is no formation of a solid phase.

environmental impacts, offering a promising solution to alleviate reliance on fossil fuels and greenhouse gas emissions.<sup>1,3–6</sup> Plasma reactors are very flexible in terms of scale and targeted feedstock/products. They are also characterised by ideal coupling to (sometimes intermittent) renewable energy sources such as solar, wind, and hydroelectric power, which become increasingly widespread and cost-effective.<sup>7,8</sup>

While plasma-based gas conversion for chemical synthesis has continuously had tangible outcomes in recent years,<sup>9–13</sup> the low product selectivity and purity is one aspect that has challenged plasma technologies in finding large-scale industrial applications. Low selectivity, often regarded as an inherent feature of applying plasma to gas conversion, is generally ascribed to the large temperature gradients observed in plasma reactors and high reactivity of plasmas.<sup>14</sup> The latter results in a wide variety of reactive species (at various distinct energies), which can generate many products. For instance, in pure  $\text{CH}_4$  plasmas, the reported products can range from  $\text{C}_{(s)}$  to fully saturated  $\text{C}_{3,4}$  olefins, alongside  $\text{H}_2$ .<sup>15,16</sup> Distinctly, in  $\text{CH}_4$  conversion, the product distribution can be promptly correlated to the bulk gas temperature in the reactor, which is in turn determined by the energy density of the plasma source.<sup>16</sup>

On the  $\text{CH}_4$  pyrolysis front for  $\text{C}_{(s)}$  and  $\text{H}_2$  production, Fulcheri *et al.*<sup>17</sup> have been leading tireless plasma research since the 1990s and in their recent work with an arc plasma ( $T_{\text{gas}}$  above 2000 °C), they successfully addressed this selectivity problem, attaining >90% conversion and >95% solid carbon selectivity.<sup>9</sup> The developed process seems robust and has already found industrial implementation with Monolith Materials using a 1 MW pilot plasma plant to co-produce 14 000 tons of carbon black and 4600 tons of hydrogen from  $\text{CH}_4$  pyrolysis per year.

A higher degree of process control is required when  $\text{CH}_4$  valorisation is pursued by carbon coupling, such as non-oxidative  $\text{CH}_4$  coupling (NOMC), instead of cracking. Selective plasma-based synthesis of  $\text{C}_2\text{H}_4$  (the most versatile light hydrocarbon, with the highest market value) at high  $\text{CH}_4$  conversions has not yet been accomplished. To date, the highest  $\text{C}_2\text{H}_4$  selectivity from  $\text{CH}_4$  coupling in plasma reactors ( $\sim 50\%$ ) was

reported by Delikonstantis *et al.*,<sup>18</sup> with the utilisation of nanosecond pulsed discharges in a co-axial reactor with an equimolar feed of  $\text{CH}_4$  and  $\text{H}_2$ . However, this level of  $\text{C}_2\text{H}_4$  selectivity was only achieved at 5 bar, with  $\text{C}_2\text{H}_2$  remaining the dominant product at lower pressures, as later confirmed by kinetic modelling.<sup>19</sup> In fact, the attainment of high  $\text{C}_2\text{H}_4$  selectivity at atmospheric pressure is impeded by the thermodynamic equilibrium of gas-phase  $\text{CH}_4$  shown in the diagrams in Fig. 1.

The equilibrium compositions clearly demonstrate that when  $\text{CH}_4$  is converted under conditions favourable to solid carbon formation (Fig. 1a), the thermodynamically favoured products are  $\text{C}_{(s)}$  and  $\text{H}_2$  (as in the work by Fulcheri *et al.*<sup>9</sup>), followed by  $\text{C}_2\text{H}_2$ , with negligible  $\text{C}_2\text{H}_4$  production. On the other hand, plasma-driven  $\text{CH}_4$  pyrolysis can be performed under conditions seeking to inhibit carbon nucleation,<sup>20</sup> which is illustrated for the ideal case in Fig. 1b (albeit some  $\text{C}_{(s)}$  formation is inevitable in reality). In this case, the dominant products are  $\text{C}_2\text{H}_2$  and  $\text{H}_2$ , and although formed in appreciable concentrations,  $\text{C}_2\text{H}_4$  can never become the major product and its occurrence has a very narrow temperature range.<sup>18,19</sup>

These thermodynamic trends allow for the interpretation of common experimental findings in  $\text{CH}_4$  plasmas. When a plasma operates under thermal or quasi-thermal conditions, as is the case for DC arc (employed by Monolith), gliding arcs and microwave plasmas, typically the main products observed are  $\text{H}_2$ ,  $\text{C}_{(s)}$  and  $\text{C}_2\text{H}_2$ , with relative concentrations that depend on specific reactor configurations. Some examples can be found in ref. 9 and 21–24. Conversely, when a non-thermal plasma (such as a dielectric barrier discharge (DBD) or pulsed corona) is employed, the primary products are  $\text{C}_2\text{H}_6$  (with some  $\text{C}_2\text{H}_4$  generation) – mostly with low energy absorption by the gas phase, leading to poor performance in terms of  $\text{CH}_4$  conversion and energy efficiencies.<sup>25,26</sup>

Undoubtedly, this analysis reveals the essential role of catalytic  $\text{C}_2\text{H}_2$  hydrogenation in plasma-based  $\text{CH}_4$  coupling for selective  $\text{C}_2\text{H}_4$  synthesis with high conversion and competitive energy efficiency. The coupling of a nanosecond pulsed  $\text{CH}_4/\text{H}_2$  plasma (with up to 40%  $\text{C}_2\text{H}_2$  yield at an energy cost of  $870 \text{ kJ mol}^{-1}$ )<sup>27,28</sup> to post-plasma hydrogenation catalysis using



a palladium-coated electrode structure has been performed by Cameli *et al.*,<sup>29</sup> demonstrating a 60% overall C<sub>2</sub>H<sub>4</sub> selectivity without external heat or further H<sub>2</sub> addition. The success of this endeavour has highlighted the potential of plasma-catalyst synergy for single-pass NOMC into C<sub>2</sub>H<sub>4</sub> in a modular fashion. Further optimisation of the structured catalyst, by employing a bimetallic Pd–Ag material, has increased the C<sub>2</sub>H<sub>4</sub> selectivity to 76% C<sub>2</sub>H<sub>4</sub>, intensifying the process performance by lowering the downstream separation cost.<sup>30</sup> Meanwhile, this approach shows great flexibility owing to the independent tuning of the plasma discharge and structured catalyst, which elicits research into different catalyst designs and compositions and alternative (perhaps simpler) catalytic setups, widening the scope of plasma-catalyst utilisation.

In this broader context, we have developed a temperature-dependent surface micro-kinetic model to investigate the selective hydrogenation of C<sub>2</sub>H<sub>2</sub>, synthesised from NOMC in a plate-to-plate nanosecond pulsed plasma reactor, using a downstream catalyst bed. The latter was packed with three different Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, with Pd loadings of 0.1, 0.5 and 1 wt%, which were activated by the heat created in the plasma. The combined (kinetic) modelling and experimental approach aims to explore the mechanisms of post-plasma C<sub>2</sub>H<sub>2</sub> hydrogenation in the presence of unreacted CH<sub>4</sub> considering the real thermal conditions in the catalyst bed downstream from the plasma zone. Building upon the current state-of-the-art,<sup>29,30</sup> our objective is to extend the applicability of Cameli's post-plasma catalytic work by demonstrating how a classic catalyst bed can be utilised to harness plasma-generated heat and drive selective C<sub>2</sub>H<sub>2</sub> hydrogenation. This strategy may open opportunities for the use of other metal catalysts in this process. Moreover, the new temperature-dependent surface micro-kinetic model aids in interpreting the reactivity results, providing insights into the adsorption/desorption mechanisms and reaction pathways that underlie the observed selectivity trends.

## 2. Experimental and computational methodology

### 2.1. Experimental setup

The reactor configuration has been described in detail in our previous work.<sup>29</sup> A schematic representation of the experimental setup is reported in Fig. 2. The reactant gas consists of 100 sccm of CH<sub>4</sub> and 100 sccm of H<sub>2</sub> feeds (regulated by two Brooks GF40 mass flow controllers) which enter the reactor from the top of the high voltage electrode. Two parallel electrodes promote electrical breakdown of the recirculating gas. The ground electrode is composed of a 3D-printed body which hosts a stainless-steel sintered filter (AmesPore, porosity 5 μm), to prevent solid carbon deposit from entering the catalytic section downstream. Thus, the catalytic step follows the gas-phase plasma activation sequentially. An NPG-18/100k (Megaimpulse Ltd) power supply is used to ignite and sustain the nanosecond-pulsed discharge (NPD) in the plate-to-plate plasma reactor. Modulation and control of the plasma signal are attained *via* a waveform



Fig. 2 Schematic of the plate-to-plate plasma reactor with a post-plasma catalytic bed for hydrogenation. Experiments carried out with 100 sccm CH<sub>4</sub> and 100 sccm H<sub>2</sub>, with three bursts at 10 kHz, 3000 p s<sup>-1</sup>, 50% voltage amplitude. The catalytic bed is composed of 200 mg Pd/Al<sub>2</sub>O<sub>3</sub> and 800 mg Al<sub>2</sub>O<sub>3</sub>.

generator (Agilent 33220A) and an oscilloscope (Wavesurfer 10, Teledyne Lecroy). The same energy pattern is applied in all experiments, with 3000 pulses per second distributed in three bursts with a frequency of 10 kHz. The applied voltage amplitude is set at 50% of the maximum attainable by the power supply. A visual representation of the energy pattern scheme is reported in the ESI† (Fig. S1). The voltage (*V*) signal is used to calculate the power (*P*) dissipated in the discharge *via* a resistive coupler (RC20, Megaimpulse), which allows assessment of the forward and reflected energy (*E*) by measuring the voltage across the circuit with a fixed impedance (*Z*), as per the equation below:

$$E = \int \frac{V^2(t)}{Z} dt$$

### 2.2. Catalyst preparation and characterisation

The catalysts used in the post-plasma region were produced *via* incipient wetness impregnation: a solution of Pd(NO<sub>3</sub>)<sub>2</sub> (Alpha Aesar) was used as the catalyst precursor and added to α-Al<sub>2</sub>O<sub>3</sub> powder (Alpha Aesar, 99.95% purity, particle size: 0.25–0.45 μm, pores volume: 0.35 mL g<sup>-1</sup>). Different dilutions of the original solution containing 10 wt% Pd were prepared to attain three metal loadings of 0.1, 0.5, and 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub>. Overnight drying at 120 °C and calcination at 600 °C for 6 h followed the impregnation step. Metal dispersion was assessed *via* pulsed H<sub>2</sub> chemisorption (Autochem II 2920, Micromeritics) of the different catalysts. The metal load is determined *via* ICP-AES (iCAP 6500, Thermo Scientific) as per the ISO 11885 methodology.

### 2.3. Downstream catalytic C<sub>2</sub>H<sub>2</sub> hydrogenation

The post-plasma catalytic hydrogenation step is performed by packing 200 mg of catalyst, diluted in 800 mg of Al<sub>2</sub>O<sub>3</sub>, into the region downstream from the filter which serves as the ground



electrode (Fig. 2). Thereby, the catalyst particles interact with the products formed *via* the recombination of plasma-generated radicals. Operando temperature monitoring was obtained through a FiSens fibre optic inserted in the catalyst bed. This fibre optic probe can measure multiple temperature points at 5 mm intervals along its axis. However, the length of the catalytic bed (8 mm) was only sufficient for two temperature measurements. The catalyst bed temperature was not independently regulated, as no external heating was applied during the experiments. Instead, the temperature was determined by two heat sources: the gas stream exiting the plasma region (*i.e.*, identical heating in all experiments, given the uniform energy profile applied in the plasma), and the exothermic hydrogenation reactions occurring at the catalyst surface. Since the contribution of hydrogenation reactions to heating varies with catalyst loading, different bed temperatures were observed across the experimental conditions. The outlet stream from the system is analysed *via* on-line gas chromatography (3000 MicroGC, Inficon), whereby a molesieve column (10 m) with backflush (3 m, Plot U) elutes H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>, whilst a Plot U column (10 m) with backflush (1 m, Plot Q) elutes C<sub>2</sub> and C<sub>3</sub> species. Internal standard N<sub>2</sub> is fed directly to the GC column, to calculate the total gas volume at the outlet of the reactor, owing to the changing number of moles in the plasma coupling and post-plasma catalytic hydrogenation reactions, as outlined below. This ensures that gas expansion/contraction is properly considered for accurate appraisal of conversion and selectivity.<sup>31</sup>



The composition of the gas stream entering the catalyst bed was assessed *via* GC measurements from experiments carried

out in the absence of catalyst. In this case, the equations used to evaluate the CH<sub>4</sub> conversion and C<sub>2</sub> product selectivity can be found in ref. 29, where we focus on these plasma-alone experiments. The GC data was used to calculate the concentrations of unreacted CH<sub>4</sub>, and formed C<sub>2</sub>H<sub>y</sub> products, which in turn were taken as a reference to isolate the contributions of plasma and catalysis in the overall conversion and selectivity from the coupled plasma-catalytic process. In this study, the more relevant metrics of C<sub>2</sub>H<sub>2</sub> conversion and C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> selectivity were calculated using the equations shown in Section 2.4(d) below, both for the experiments (*via* GC analysis of the outlet gas treated by plasma and catalysis) and the model (using calculated densities). The experimental plasma-alone concentrations were also used as input in the micro-kinetic model (initial partial pressures), as explained below.

## 2.4. Surface kinetic model

**(a) Gas composition, species and reactions included in the model.** The initial gas composition used in the model was identical to that measured at the outlet of the plasma reactor. The partial pressures of the gas were calculated and inserted in the model as follows: H<sub>2</sub> = 0.528; CH<sub>4</sub> = 0.300; C<sub>2</sub>H<sub>2</sub> = 0.160; C<sub>2</sub>H<sub>4</sub> = 0.010 and C<sub>2</sub>H<sub>6</sub> = 0.002 (the reference pressure is 1 bar).

The species and reactions considered in the surface kinetic model are outlined in Table 1.

Our model is based on this reaction network and the Pd(111) energetics derived from density functional theory (DFT) calculations performed by Nørskov *et al.*<sup>32</sup> These DFT calculations were carried out using Quantum Espresso, with the exchange-correlation contribution to the electronic energy approximated by the BEEF-vdW functional. We refer to the cited study for additional DFT details. The reaction network consists of adsorption and desorption of the gas-phase molecules – reactions r<sub>1</sub>–r<sub>6</sub> (with H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> dissociating upon

**Table 1** Species included in the model (the asterisk, \*, denotes an empty surface site, while adsorbed species are followed by \*), reaction network with an indication of the initial, transition and final states and respective activation and reaction energies in eV

Reaction	Initial state $\rightleftharpoons$ transition state $\rightleftharpoons$ final state	Surface species	Activation energy (eV)	Reaction energy (eV)
r <sub>1</sub>	H <sub>2</sub> (g) + 2 * $\rightleftharpoons$ *-H-H-* + * $\rightleftharpoons$ H* + H*	H*	0.28	-0.83
r <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> (g) + * $\rightleftharpoons$ C <sub>2</sub> H <sub>2</sub> -* $\rightleftharpoons$ C <sub>2</sub> H <sub>2</sub> *	C <sub>2</sub> H <sub>2</sub> *	0.00	-1.67
r <sub>3</sub>	C <sub>2</sub> H <sub>4</sub> (g) + * $\rightleftharpoons$ C <sub>2</sub> H <sub>4</sub> -* $\rightleftharpoons$ C <sub>2</sub> H <sub>4</sub> *	C <sub>2</sub> H <sub>4</sub> *	0.00	-0.76
r <sub>4</sub>	C <sub>2</sub> H <sub>6</sub> (g) + 2 * $\rightleftharpoons$ *-C <sub>2</sub> H <sub>5</sub> -H-* $\rightleftharpoons$ C <sub>2</sub> H <sub>5</sub> * + H*	C <sub>2</sub> H <sub>5</sub> *	1.18	0.18
r <sub>5</sub>	C <sub>2</sub> H <sub>6</sub> (g) + 2 * $\rightleftharpoons$ *-CH <sub>3</sub> -CH <sub>3</sub> -* $\rightleftharpoons$ CH <sub>3</sub> * + CH <sub>3</sub> *	CH <sub>3</sub> *	2.89	0.60
r <sub>6</sub>	CH <sub>4</sub> (g) + 2 * $\rightleftharpoons$ *-CH <sub>3</sub> -H-* $\rightleftharpoons$ CH <sub>3</sub> * + H*	CH <sub>3</sub> *	1.29	0.31
r <sub>7</sub>	C <sub>2</sub> H <sub>2</sub> * + H* $\rightleftharpoons$ *C <sub>2</sub> H <sub>2</sub> -H-* $\rightleftharpoons$ C <sub>2</sub> H <sub>3</sub> * + *	C <sub>2</sub> H <sub>3</sub> *	0.95	0.05
r <sub>8</sub>	C <sub>2</sub> H <sub>3</sub> * + H* $\rightleftharpoons$ *C <sub>2</sub> H <sub>3</sub> -H-* $\rightleftharpoons$ C <sub>2</sub> H <sub>4</sub> * + *	C <sub>2</sub> H <sub>4</sub> *	0.64	-0.48
r <sub>9</sub>	C <sub>2</sub> H <sub>4</sub> * + H* $\rightleftharpoons$ *C <sub>2</sub> H <sub>4</sub> -H-* $\rightleftharpoons$ C <sub>2</sub> H <sub>5</sub> * + *	C <sub>2</sub> H <sub>5</sub> *	0.85	0.11
r <sub>10</sub>	C <sub>2</sub> H <sub>5</sub> * + * $\rightleftharpoons$ *CH <sub>3</sub> -CH <sub>2</sub> -* $\rightleftharpoons$ CH <sub>3</sub> * + CH <sub>2</sub> *	CH <sub>3</sub> *	2.18	0.74
r <sub>11</sub>	C <sub>2</sub> H <sub>4</sub> * + * $\rightleftharpoons$ *CH <sub>2</sub> -CH <sub>2</sub> -* $\rightleftharpoons$ CH <sub>2</sub> * + CH <sub>2</sub> *	CH <sub>2</sub> *	1.89	1.17
r <sub>12</sub>	C <sub>2</sub> H <sub>3</sub> * + * $\rightleftharpoons$ *CH <sub>2</sub> -CH-* $\rightleftharpoons$ CH <sub>2</sub> * + CH*	CH <sub>2</sub> *	1.47	0.34
r <sub>13</sub>	C <sub>2</sub> H <sub>2</sub> * + * $\rightleftharpoons$ *CH-CH-* $\rightleftharpoons$ CH* + CH*	CH*	1.63	0.04
r <sub>14</sub>	CH <sub>3</sub> * + * $\rightleftharpoons$ *CH <sub>2</sub> -H-* $\rightleftharpoons$ CH <sub>2</sub> * + H*	CH <sub>2</sub> *	1.13	0.32
r <sub>15</sub>	CH <sub>2</sub> * + * $\rightleftharpoons$ *CH-H* $\rightleftharpoons$ CH* + H*	CH*	0.79	-0.35
r <sub>16</sub>	CH* + * $\rightleftharpoons$ *C-H* $\rightleftharpoons$ C* + H*	C*	1.42	0.38
r <sub>17</sub>	H <sub>2</sub> (g) + C <sub>2</sub> H <sub>4</sub> * + * $\rightleftharpoons$ *-H-C <sub>2</sub> H <sub>5</sub> * $\rightleftharpoons$ C <sub>2</sub> H <sub>5</sub> * + H*	C <sub>2</sub> H <sub>5</sub> *	1.44	-0.72



adsorption); hydrogenation and de-hydrogenation – reactions  $r_7$ – $r_9$ ,  $r_{14}$ – $r_{16}$ ; and surface dissociation and recombination – reactions  $r_{10}$ – $r_{13}$  and  $r_{17}$ . In turn, the model provides quantitative information on catalyst activity and selectivity as a function of temperature. The relevant equations and formulas are presented in the following sections.

**(b) Numerical details, governing equations and model solution.** The micro-kinetic surface model was constructed using the CSTR (continuously stirred tank reactor) approach, which assumes perfect mixing throughout the simulation, with species densities and coverages being considered uniform within the reactor volume. The changes in the number density of gas-phase species (Table 1) as a function of time were calculated using the following balance equation.

$$\frac{\partial n_s}{\partial t} = n_{\text{sites}} \times \sum_{i,\text{cat}} \left[ \left( C_{s,i}^r - C_{s,i}^f \right) \times r_i \right] + \frac{n_{s,\text{in}} \times v_{\text{in}}}{V_{\text{CSTR}}} + \frac{n_{s,\text{out}} \times v_{\text{out}}}{V_{\text{CSTR}}}$$

where  $n_s$  is the number density of species  $s$  and  $t$  is the simulation time. The first term on the right side is related to the change in  $n_s$  due to surface reactions at the catalyst, with  $C_{s,i}^r$  and  $C_{s,i}^f$  being the stoichiometric coefficients of species  $s$  in reaction  $i$  (reverse, r, and forward, f), and  $r_i$  being the reaction rate (expressed in  $\text{s}^{-1}$ ). This term must be multiplied by the total volumetric density of surface sites  $n_{\text{sites}}$  (in  $\text{cm}^{-3}$ , with calculation details given in Section S2 in the ESI<sup>†</sup>) to have the rate involving gas species correctly expressed in  $\text{cm}^{-3} \text{s}^{-1}$ . The approach utilised to calculate the rates will be presented later in this section, following the description of the balance equation for surface species. The second and third terms represent the change in number density due to gas molecules entering and exiting the reactor, respectively. In these,  $n_{s,\text{in}}$  is the species density at the inlet and  $n_{s,\text{out}}$  at the outlet (note that in a CSTR model,  $n_{s,\text{out}}$  equals the species density  $n_s$  in the reactor),  $V_{\text{CSTR}}$  is the gas volume in the reactor, and  $v_{\text{in}}$  and  $v_{\text{out}}$  are the volumetric flow rate entering and exiting the reactor, respectively.

The volumetric flow rate of the exiting gas ( $v_{\text{out}}$ ) used in the equation above is calculated as follows, so that the total pressure ( $p_{\text{total}}$ , expressed in Pascal here for unit consistency) in the reactor is maintained constant at ambient pressure in all simulations.

$$v_{\text{out}} = v_{\text{in}} + \frac{V_{\text{CSTR}} \times k_b \times T}{p_{\text{total}}} \times n_{\text{sites}} \times \sum_{i,\text{cat}} \left[ \left( C_{s,i}^f - C_{s,i}^r \right) \times r_i \right]$$

In which  $k_b$  is the Boltzmann constant and  $T$  is the temperature. In practice, this equates the exiting volumetric flow rate to the incoming flow rate plus the change in volume resulting from catalytic reactions.

Similar to the balance equations above for the gas-phase species, the changes in the surface coverage ( $\theta_s$ ) of surface species  $s$  (Table 1) as a function of time  $t$  are described using the following balance equation, in which  $C_{s,i}^f$  and  $C_{s,i}^r$  are the stoichiometric coefficients of species  $s$  in reaction  $i$ , with the forward (f) and reverse (r) reactions, and  $r_i$  is the reaction rate of the surface reactions (again expressed in  $\text{s}^{-1}$ ).

$$\frac{\partial \theta_s}{\partial t} = \sum_{i,\text{cat}} \left[ \left( C_{s,i}^f - C_{s,i}^r \right) \times r_i \right]$$

The reaction rate ( $r_i$ ) in the above equations depends on the rate coefficient, species activity and reaction stoichiometry, and is defined as follows.

$$r_i = k_{i,f} \prod_s (a_s)^{C_{s,i}^f} - k_{i,r} \prod_s (a_s)^{C_{s,i}^r}$$

where  $k_{i,f}$  and  $k_{i,r}$  are the forward and reverse reaction rate coefficients, respectively, and  $a_s$  is the activity of species  $s$ . The latter may be the partial pressure of gas phase species ( $p_s$ , divided by  $p_{\text{total}}$  to maintain  $k_{i,f}$  and  $k_{i,r}$  in units of  $\text{s}^{-1}$ ) in surface reactions, or the fractional coverage ( $\theta_s$ ) for surface species. Note that number densities and partial pressures are interconvertible *via* the ideal gas law. The rate coefficients  $k_{i,f}$  and  $k_{i,r}$  are calculated using transition state theory with the following equation.

$$k = \frac{k_b T}{h} \times e^{\left( -\frac{\Delta G^\ddagger}{RT} \right)} = \frac{k_b T}{h} \times e^{\left( -\frac{\Delta H^\ddagger}{RT} \right)} \times e^{\left( \frac{\Delta S^\ddagger}{R} \right)}$$

In this,  $h$  is Planck's constant,  $R$  is the universal gas constant, and  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the differences in Gibbs free energy, enthalpy and entropy, respectively, between the initial state and the transition state (see Table 1). The inputs for enthalpy and entropy differences and their respective temperature-dependent thermodynamic corrections are discussed in the following section.

The model is solved using an in-house python code which was written for applications in post-plasma and plasma catalysis. A version of this code is quoted in Section S3 in the ESI<sup>†</sup>. The input data required to run the code include the reaction network (see Table 1), the formation enthalpies and rotational and vibrational wavenumbers of species in the model (see Table S1 in Section S4 of the ESI<sup>†</sup>), and the gas-phase species parameters for the Shomate equation (taken from the NIST database).

**(c) Assumptions and approximations.** This study concerns a pure post-plasma catalysis micro-kinetic model with only stable gaseous molecules present in the gas flow, because plasma-derived radicals rapidly recombine and are thus absent in the catalyst bed. The construction of the model is based on a CSTR approach, which assumes that the densities of the gas species and surface coverages are uniformly distributed over the reactor volume.<sup>33,34</sup> The CSTR choice is intended to achieve a manageable computational complexity, whilst solving the model inexpensively for the three Pd loadings across the wide temperature range investigated in this work. The applicability of this CSTR model (over a PFR model, plug flow reactor) is also corroborated by the relatively large Péclet number (Pe) expected for packed bed systems.<sup>35</sup> We believe that the PFR approach could improve the accuracy of the model's predictions by accounting for the changing concentrations across the catalyst bed. However, due to the packing of solids in the reactor utilised in the experiments (*i.e.*, non-trivial gas flow patterns and large Pe), both axial and radial gas mixings are significant, ultimately rendering the PFR approach also approximative. In a PFR configuration, the conversion would likely be higher than in our CSTR model because the latter assumes perfect mixing,



thus immediately leading to lower concentrations. In turn, this causes positive order reactions to proceed at a lower rate, which yields a lower conversion for the same residence time as a PFR model.

The temperature of the catalyst bed is also assumed to be uniform throughout the reactor and the model assumes thermal equilibrium between the gas phase and catalyst surface. While temperature gradients will exist in the reactor, their assessment would require a higher-dimensional model incorporating heat transfer mechanisms and gas flow dynamics. Such analysis, though valuable, extends beyond the capabilities of our current 0D framework, which focuses on capturing the chemical kinetic behaviour of the system.

No formation of solid products at the catalyst's surfaces (polymers and carbon black) is considered in the model. Whilst very interesting, such modelling endeavour would rely on DFT data which is presently unavailable and would require a higher dimensional model, which is not within the scope of this study. With respect to the surface reactions, the model calculates rate coefficients based on transition state theory, as explained in the above section, whilst employing DFT-derived activation barriers as input in the rate expressions. While this approach yields more accurate rates than those estimated using sticking coefficients or reaction barriers,<sup>33</sup> it is inherently limited by the availability and quality of DFT data. In this study, all activation energies and frequencies (used to calculate entropies and temperature-dependent corrections) were extracted from the work by Nørskov *et al.*<sup>32</sup> who have described the dehydrogenation of C<sub>2</sub>H<sub>6</sub> over many close-packed metal surfaces (see Table S1 in Section S4 of the ESI†).

To account for the activity of the Pd(100) and Pd(211) facets (which may be considerable depending on nanoparticle morphology and particle size),<sup>36,37</sup> we performed a sensitivity analysis by applying the adsorption energies for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> on Pd(100) and Pd(211) in our micro-kinetic model (see Table S2 in the ESI†). These facets were chosen based on their respective lowest and highest reported activities in the literature.<sup>36</sup> Due to the lack of comprehensive DFT data for all reaction species on Pd(100) and Pd(211), we retained our original reaction network developed for Pd(111) and substituted the available adsorption energies for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. The details of this analysis can be found in Section S5 in the ESI.† The results indicate that Pd(100) is by far the least active facet, with no observable C<sub>2</sub>H<sub>2</sub> conversion below ~600 °C (Fig. S2a, ESI†). Conversely, Pd(211) is an overly active surface, fully hydrogenating C<sub>2</sub>H<sub>2</sub> to C<sub>2</sub>H<sub>6</sub> at temperatures as low as 90 °C (Fig. S2b, ESI†). These trends, albeit inherently qualitative due to the incomplete DFT datasets, do not align with our experimental results (see Fig. 3 and 4 in Section 3). Thus, we conclude that Pd(111) is the most appropriate facet to model C<sub>2</sub>H<sub>2</sub> hydrogenation, for the conditions under study in this work.

**(d) Conversion and selectivity.** For both model and experiments, the overall C<sub>2</sub>H<sub>2</sub> conversion ( $\chi_{\text{C}_2\text{H}_2}$ ), and C<sub>2</sub>H<sub>4</sub> ( $S_{\text{C}_2\text{H}_4}$ ) and C<sub>2</sub>H<sub>6</sub> ( $S_{\text{C}_2\text{H}_6}$ ) selectivity, can be derived using the following

equations.

$$\chi_{\text{C}_2\text{H}_2} (\%) = \left( 1 - \frac{\text{C}_2\text{H}_2^{\text{out}} \times \nu^{\text{out}}}{\text{C}_2\text{H}_2^{\text{in}} \times \nu^{\text{in}}} \right) \times 100 (\%)$$

$$S_{\text{C}_2\text{H}_4} (\%) = \frac{\text{C}_2\text{H}_4^{\text{out}} \times \nu^{\text{out}}}{\text{C}_2\text{H}_2^{\text{in}} \times \nu^{\text{in}} - \text{C}_2\text{H}_2^{\text{out}} \times \nu^{\text{out}}} \times 100 (\%)$$

$$S_{\text{C}_2\text{H}_6} (\%) = \frac{\text{C}_2\text{H}_6^{\text{out}} \times \nu^{\text{out}}}{\text{C}_2\text{H}_2^{\text{in}} \times \nu^{\text{in}} - \text{C}_2\text{H}_2^{\text{out}} \times \nu^{\text{out}}} \times 100 (\%)$$

where in the experiments, C<sub>2</sub>H<sub>2</sub><sup>out</sup> represents the volume fraction of C<sub>2</sub>H<sub>2</sub> exiting the reactor (measured by GC in the coupled plasma and catalysis experiments) and  $\nu^{\text{out}}$  is the outlet volumetric flow rate. Likewise, C<sub>2</sub>H<sub>2</sub><sup>in</sup> represents the inlet C<sub>2</sub>H<sub>2</sub> volume fraction (reference value, measured in the absence of catalyst, as explained above) and  $\nu^{\text{in}}$  is the inlet volumetric flow rate. In the model, C<sub>2</sub>H<sub>2</sub><sup>out</sup> and  $\nu^{\text{out}}$  are the C<sub>2</sub>H<sub>2</sub> density and volumetric flow rate at steady state in the outflow, C<sub>2</sub>H<sub>2</sub><sup>in</sup> and  $\nu^{\text{in}}$  are the initial C<sub>2</sub>H<sub>2</sub> density and volumetric flow rate, respectively. For selectivity, C<sub>2</sub>H<sub>4</sub><sup>out</sup> and C<sub>2</sub>H<sub>6</sub><sup>out</sup> are GC-derived volume fractions of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> in the outlet stream in the experiments, respectively; while in the model these are the densities of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> in steady state, respectively (also corresponding to the outflow).

Additionally, the modelled densities are also used to calculate CH<sub>4</sub> ( $S_{\text{CH}_4}$ ) selectivity using the equation below, with CH<sub>4</sub><sup>out</sup> being the CH<sub>4</sub> density in the steady state (outflow) and CH<sub>4</sub><sup>in</sup> being the initial CH<sub>4</sub> density.

$$S_{\text{CH}_4} (\%) = \frac{\text{CH}_4^{\text{out}} \times \nu^{\text{out}} - \text{CH}_4^{\text{in}} \times \nu^{\text{in}}}{\text{C}_2\text{H}_2^{\text{in}} \times \nu^{\text{in}} - \text{C}_2\text{H}_2^{\text{out}} \times \nu^{\text{out}}} \times 100 (\%)$$

The volumetric flow rates at the inlet  $\nu^{\text{in}}$  and outlet  $\nu^{\text{out}}$  are explicitly included in these equations to account for the effect of pressure changes due to gas expansion/contraction (as explained above) and temperature increase during the reaction.<sup>38</sup>

## 3. Results and discussion

### 3.1. Plasma reactor for CH<sub>4</sub> coupling – experimental and modelled results

The gas-phase chemistry within the NPD reactor has been thoroughly characterised in our previous studies.<sup>19,27,29</sup> A comprehensive reaction mechanism has revealed that at atmospheric pressure, CH<sub>4</sub> coupling predominantly produces C<sub>2</sub>H<sub>2</sub> through the stepwise dehydrogenation of C<sub>2</sub>H<sub>6</sub>, which itself is formed *via* the recombination of CH<sub>3</sub> radicals.<sup>19,20,26,39</sup> Unsurprisingly, CH<sub>3</sub> species are the most abundant carbon-based radicals generated from CH<sub>4</sub> dissociation *via* electron-impact reactions. The principal mechanism for the coupling of electron energy to gas-phase heating involves electron-impact vibrational excitation of CH<sub>4</sub> and H<sub>2</sub> molecules followed by rapid vibrational–translational (VT) relaxation reactions.<sup>40</sup> The gas temperature within this NPD plasma can reach up to 1500 °C in the vicinity of the discharges, which in turn



promotes dehydrogenation of  $C_2H_6$  to  $C_2H_4$  (but also to  $C_2H_5$  and  $C_2H_3$  radicals) and ultimately to  $C_2H_2$ .<sup>19</sup>

As a result, this plasma configuration achieves a  $C_2H_2$  selectivity of approximately 83% under the specified operating conditions (*i.e.*, three bursts at 10 kHz, 3000 pulses  $s^{-1}$ ). The conversion of  $CH_4$ , co-fed with an equimolar amount of  $H_2$ , averages around 46%. The selectivity for  $C_2H_4$  and  $C_2H_6$  is about 5% and 1%, respectively. The remaining percentage is attributed to small quantities of unquantified hydrocarbon products (*e.g.*,  $C_3$  and  $C_4$  species) and solid carbon, which amounts to about 3% of the converted  $CH_4$  in weight.

### 3.2. Post-plasma catalytic hydrogenation of $C_2H_2$ to $C_2H_4$

The high  $C_2H_2$  selectivity attained in this NPD reactor enables effective tandem hydrogenation to  $C_2H_4$ , which is catalysed by the  $Pd/Al_2O_3$  material placed downstream from the plasma discharge. This strategy allows for the flexible adjustment of the product distribution in a modular fashion, which can be tailored to meet oscillatory market demands. Notably, the catalytic hydrogenation reaction is solely activated by the hot gas flowing from the discharge zone, and it is self-sustained by its exothermic nature (*i.e.*,  $C_2H_2 + H_2 \rightarrow C_2H_4$ , with  $\Delta H^0 = +175.9 \text{ kJ mol}^{-1}$ ; and  $C_2H_2 + 2H_2 \rightarrow C_2H_6$ , with  $\Delta H^0 = +311.5 \text{ kJ mol}^{-1}$ ). However, the three Pd loadings within the  $Pd/Al_2O_3$  catalyst, along with the dispersion degree of the active metal, promote varying  $C_2H_2$  conversion and  $C_2H_4/C_2H_6$  product distribution trends within different temperature ranges. Consequently, both the reaction temperatures and kinetics may differ with the catalyst used. In the subsequent sections, we discuss the reactivity results for each catalyst within the temperature window measured in the experiments and apply our model to extrapolate the selectivity behaviour at higher and lower temperatures. Whenever possible, we compare the model predictions with our experimental data to reinforce the credibility of these temperature extrapolations.

**(a)  $C_2H_2$  conversion.** Both experimental and modelled results indicate that the reactivity of the  $Pd/Al_2O_3$  catalysts is influenced by the Pd loading and the dispersion degree of Pd atoms within the material. As seen in Fig. 3, the catalysts with higher Pd loading (and greater metal dispersion) exhibit a lower temperature threshold for activation, *i.e.*, initiation of  $C_2H_2$  hydrogenation. For the 1% Pd catalyst (with a dispersion of 10%), the onset of  $C_2H_2$  conversion occurs between 110 and 120 °C in the experiments. However, this activation temperature range increases to 130–137 °C and 135–144 °C as the Pd loading decreases to 0.5% and 0.1%, with 7% and 33% dispersion, respectively. Note that the dispersion is not determined by the loading, but only related to the preparation method. The lower  $C_2H_2$  conversion onsets observed for the higher Pd loadings can be attributed to the enhanced rates of  $C_2H_2$  and  $H_2$  adsorption due to larger amounts of active sites. In turn, these higher rates give rise to more intense surface heating of the catalysts with higher loading (due to the exothermic nature of  $C_2H_2$  hydrogenation), further accelerating the reaction rates and conversion. These effects are determined by both higher loading and higher metal dispersion, which decrease the

activation temperature threshold, explaining the similar activity of the 0.5 and 0.1% loadings.

Fig. 3 also shows that the modelled results align well with the experimental data points in the region where the temperature is exclusively dictated by the plasma discharge and the exothermic heat from the hydrogenation reaction. The lack of control over the experimental temperature does not allow mapping of the catalyst activity across different temperatures in these experiments. However, these results prove that the post-plasma catalytic setup is suitable for  $C_2H_2$  hydrogenation, even at low metal loading, as all catalysts attain  $C_2H_2$  conversion above 90% under the experimental conditions at the steady state. The modelled trends confirm the catalysts' high activity for  $C_2H_2$  hydrogenation and can give an indication of the behaviour at higher temperatures. The modelled  $C_2H_2$  conversion trends in the 80 to 750 °C temperature range can be found in Fig. S3 in the ESI† (Section S6, ESI†).

Nonetheless, the model underestimates  $C_2H_2$  conversion at lower temperature for the 0.1%  $Pd/Al_2O_3$  and 0.5%  $Pd/Al_2O_3$  catalysts, and it suggests a sharp transition from nil to complete conversion at 137 and 142 °C, whilst experimental data show a more gradual increase. These discrepancies can be ascribed to the temperature input used in the model. The model relies on the gas temperature at the catalyst active sites, while in the experiments, the fibre optic temperature sensor is positioned along the axial axis of the catalytic bed; and it is reasonable to assume that the catalyst surface may be warmer than the surrounding gas due to the exothermic reactions occurring at the active sites. Indeed, it would be very insightful to investigate the heat transfer from the warmer catalyst surface to the gas phase and the temperature gradient in the reactor, as well as the impact of the exothermic chemical reactions, by solving an energy balance equation. However, the current model is unable to capture these effects, as the dynamics of heat transfer and gas flow cannot be accurately considered in this zero-dimensional model. While this is outside the scope of this study, in our future work, we plan the construction and application of a dedicated higher-dimensional computational

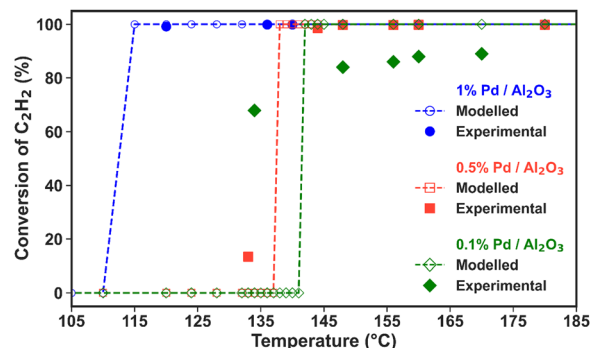


Fig. 3 Experimental and modelled  $C_2H_2$  conversion as a function of temperature (average temperature measured in the catalyst bed and assumed to be identical for solid and gas phases) for the three  $Pd/Al_2O_3$  catalysts (see the legend). The number of experimental data points (solid markers) is different for each catalyst.



fluid dynamics and surface kinetics model to explore these aspects as well.

**(b) Product selectivity.** We have applied the model to calculate the product selectivity from  $C_2H_2$  hydrogenation over a wide range of temperature (up to  $750\text{ }^\circ\text{C}$ ), as depicted in Fig. 4(a)–(c). Within the temperature range registered in the experiments (indicated by the yellow rectangles in Fig. 4), the model predictions agree well with the experimental results (obtained as a single data point for each set of catalytic material) for the 0.1% Pd catalyst (Fig. 4a). This agreement is however less accurate for the other two catalysts. At lower temperatures, the model predicts that  $C_2H_4$  is the main product when the reaction begins, as it is thermodynamically favoured over further hydrogenations to  $C_2H_6$  (a mechanistic analysis is provided in the following section). Over the 0.1% Pd catalyst, the calculated  $C_2H_4$  selectivity peaks at 83% (with 17%  $C_2H_6$  selectivity) at  $142\text{ }^\circ\text{C}$ , *i.e.*, the onset of the activation temperature, while the experimental values are 65% and 31%,



Fig. 4 Experimental and modelled  $C_2H_4$ ,  $C_2H_6$  and  $CH_4$  selectivity as a function of temperature (average temperature measured in the catalyst bed and assumed to be identical for solid and gas phases) for the (a) 0.1%, (b) 0.5%, and (c) 1% Pd/ $Al_2O_3$  catalysts. The solid markers correspond to the experimental selectivity measured within the temperature range highlighted by the shaded area (yellow rectangle) on the graph. The dashed lines and hollow markers show the trends predicted by the model.

respectively (though with relatively large error bars). Furthermore, the model suggests an inversion in  $C_2H_4$  and  $C_2H_6$  selectivity as the temperature increases, with  $C_2H_6$  becoming dominant due to prompt over-hydrogenation of  $C_2H_4$ . However, this could not be validated experimentally because no external catalyst heating was applied in the experiments; hence only one data point is available, corresponding to the temperature reached by plasma heating (and the exothermic hydrogenation reactions).

All catalysts attain near-complete  $C_2H_2$  conversion in the experiments (90% for 0.1% Pd/ $Al_2O_3$  and  $>99\%$  for 0.5 and 1% Pd/ $Al_2O_3$ , see Fig. 3), which is advantageous for downstream separation steps. Thus, under these conditions, the Pd loading is the only independent variable controlling the  $C_2H_4$  selectivity. Notably, the highest  $C_2H_4$  yield (*i.e.*, 12%, at  $142\text{ }^\circ\text{C}$ ) is achieved by 0.1% Pd/ $Al_2O_3$ , which favours higher  $C_2H_4$  selectivity despite a slightly lower  $C_2H_2$  conversion.

The  $C_2H_4$  yield is the major metric of successful  $CH_4$  non-oxidative coupling, as it is the most valuable product. Its maximum value is determined by the catalytic  $C_2H_2$  conversion and the corresponding selectivity for  $C_2H_4$ , since  $CH_4$  conversion is driven solely by the plasma discharge. While the latter also affects the  $C_2H_4$  yield, it does not vary with the studied Pd loadings, as the amount of  $C_2H_2$  produced in the plasma region remains constant across the different Pd loadings in the post-plasma region. Similarly, the temperature of the gas exiting the plasma zone and entering the catalytic bed is identical in all experiments, as it is purely controlled by the plasma energy (uniform in all experiments). Our reactor configuration, where the catalytic bed is integrated in the post-plasma region without external heating, creates an inherent coupling between reaction temperature and catalyst loading. While the temperature of the gas exiting the plasma zone is constant across all experiments, the bed temperature varies with Pd loading due to the exothermic hydrogenation reactions. Although experiments at lower catalyst loadings could be useful to investigate incomplete conversion regimes, we focus here on conditions achieving full  $C_2H_2$  conversion, which is critical for maximising  $C_2H_4$  yield in industrial applications.

The modelled trend of decreasing  $C_2H_4$  selectivity and increasing  $C_2H_6$  selectivity upon rising temperature is qualitatively consistent for all three catalysts, with the key difference being the temperature at which  $C_2H_6$  becomes the dominant product, see Fig. 4(a)–(c). This shift occurs at lower temperatures with increasing metal loading, indicating higher catalyst activity, and is detrimental for the desired overall  $C_2H_4$  selectivity. Beyond this point,  $C_2H_6$  selectivity becomes 100% due to  $C_2H_4$  over-hydrogenation, until the temperature reaches about  $500\text{ }^\circ\text{C}$ , where another shift in reactivity occurs, leading to rapidly rising production of  $CH_4$  and a minor region of  $C_2H_4$  formation. The thermodynamic mechanisms driving these observations are discussed in detail in the following section.

However, these higher temperatures exceed the operational range of the catalyst bed, which is limited by the temperature of the gas exiting the discharge region and the exothermic heat of the reaction. The experimental operating window of the catalyst



bed (highlighted by the yellow areas in Fig. 4) corresponds to temperatures recorded over the entire hydrogenation experiment and correlate with the gas composition measured at the same acquisition time. The fast reaction kinetics results in a quick temperature rise and onset of steady-state conditions (within 10 min of plasma ignition), which does not allow the GC analysis to capture the transient composition in detail, as shown in Fig. 3. No substantial temperature increase is observed after reaching the steady-state, and all highlighted areas correspond to a relatively narrow temperature range. Given the scale difference between the modelled and experimental temperature ranges, the selectivity data from the experiments would largely overlap. For that reason, we only report one experimental point for the selectivity, as representative of the steady-state conditions.

In the experiments with the 0.1% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, 65% C<sub>2</sub>H<sub>4</sub> selectivity was achieved from C<sub>2</sub>H<sub>2</sub> hydrogenation, compared to 31% C<sub>2</sub>H<sub>6</sub> selectivity, between 140 and 175 °C (Fig. 4a), as also mentioned above. This is consistent with our previous results and other C<sub>2</sub>H<sub>2</sub> hydrogenation reports in the literature.<sup>29,41–44</sup> However, this state is reached within 5 min of plasma ignition and changes over longer periods, as the catalyst bed temperature rises to ~170 °C and oligomerisation products begin to form from C<sub>2</sub>H<sub>2</sub> conversion. This is accompanied by a drastic decline in C<sub>2</sub> product detection in the experiments. As previously explained, oligomerisation reactions leading to solid products are not included in the model, which focuses instead on the kinetics of gaseous H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub> (besides the short-lived surface species).

Nonetheless, the formation of oligomerisation by-products is the primary reason for the reduced C<sub>2</sub> selectivity observed experimentally at higher temperatures. On this note, the carbon balance in the system drops from 91% at the start of the hydrogenation processes (at the lower end of the temperature window) to less than 70% after about 50 minutes, when the temperature of the gas-phase is expected to exceed 200 °C. Whilst these solid deposits on the catalyst surface may affect the activity, the time-on-stream data of the product gas composition shows a relatively constant trend over approximately 40 minutes (see Fig. S4 in the ESI†), suggesting that no major catalyst deactivation (*via* sintering, for instance) occurs.

As observed in Fig. 4(b) and (c), for both higher Pd catalyst loadings, C<sub>2</sub>H<sub>6</sub> was detected as the primary product in the experiments, immediately after the reaction began. In fact, practically no C<sub>2</sub>H<sub>4</sub> was detected when the 1% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was tested, with C<sub>2</sub>H<sub>6</sub> emerging as the sole product at ~60% selectivity. These results are consistent with model predictions (though only at somewhat higher temperatures for the C<sub>2</sub>H<sub>4</sub> selectivity), which suggest that C<sub>2</sub>H<sub>4</sub> hydrogenation to C<sub>2</sub>H<sub>6</sub> occurs at lower temperatures upon increasing Pd loading. In summary, the temperature range where C<sub>2</sub>H<sub>4</sub> is the dominant hydrogenation product shifts to lower temperatures and narrows as the Pd loading is increased. For both catalysts, the experimental and modelled results show close alignment in terms of C<sub>2</sub>H<sub>6</sub> selectivity, while the C<sub>2</sub>H<sub>4</sub> selectivity is over-estimated by the model in the low-temperature regime: below

240 °C for the 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and below 210 °C for 1% Pd/Al<sub>2</sub>O<sub>3</sub>.

This discrepancy may be partially related to the difference in temperature considerations – the surface temperature input in the model *versus* bulk bed temperature measured in experiments, as explained above. However, the most likely factor contributing to selectivity disagreement is the extensive formation of oligomeric carbonaceous deposits (green oil)<sup>36</sup> at full C<sub>2</sub>H<sub>2</sub> conversion and temperatures above 170 °C, facilitated by the higher Pd loadings. Evidence supporting this mechanism is found in the calculated carbon balance of ~76% in the experiments with both 0.5% and 1% Pd catalysts, while the hydrogen balance is greater than 91%. This indicates the formation of species with high C/H ratios, typical of oligomerisation compounds, which are not included in our model.

Additionally, an approximative evaluation of the potential impact of carbon deposition in the form of C<sub>(s)</sub> was conducted in the model by analysing the CH\* + \* → C\* + H\* reaction rate (r<sub>16</sub>). The results show that the rate of this reaction is relatively negligible across the temperature range investigated in this study (see Fig. S5 in Section S8 of the ESI†). This suggests that deposition of C<sub>(s)</sub> particles is very unlikely and cannot cause the observed differences between model predictions and the experimental data in this study. Instead, the analysis indicates that the dominant pathway is the sequential hydrogenation of CH<sub>x</sub> surface species (see Section 4), which are converted to CH<sub>4</sub> above 500 °C (rather than dehydrogenated into solid carbon).

Also noteworthy, the formation of Pd carbide during C<sub>2</sub>H<sub>2</sub> hydrogenation is closely associated with the deposition of carbonaceous oligomers on the catalyst surface.<sup>44</sup> While the present model is not able to explicitly account for PdC<sub>x</sub> phases, their inclusion could, on the one hand, alter the Pd energetics of the surface reactions, leading to shifts in the model predictions. On the other hand, the model may see accumulation of PdC<sub>x</sub> species on the Pd surface, leading to lower C<sub>2</sub>H<sub>4</sub> and (especially) C<sub>2</sub>H<sub>6</sub> product selectivity and in turn smaller discrepancies between model and experiment. However, a detailed treatment of Pd carbide effects would require dedicated DFT data (which is not available, to the best of our knowledge) and potentially higher-dimensional modelling, beyond the scope of this study, but it represents an important direction for future research. Nevertheless, as discussed, we believe the deposition of high molecular weight oligomerisation solids on the catalyst remains the primary contributor to the disagreement in selectivity.

Finally, the morphology and size of the synthesised particles should be consistent across all tested catalysts (0.1%, 0.5%, and 1% Pd/Al<sub>2</sub>O<sub>3</sub>), as these were prepared *via* the same wetness impregnation method. Moreover, identical Al<sub>2</sub>O<sub>3</sub> support particles and dilution beads were used in all experiments, further ensuring uniformity. SEM images of the spent catalysts (Fig. S6 in Section S9 of the ESI†) confirm no observable differences in particle size or morphology, indicating that these factors are not the reason for the varying catalytic performances across the three investigated Pd loadings.

Essentially, these results highlight the dual impact of higher Pd loadings: (i) they promote prompt over-hydrogenation to



$C_2H_6$  by lowering the temperature at which sequential surface hydrogenation reactions occur (namely from  $C_2H_2^*$  to  $C_2H_3^*$  to  $C_2H_4^*$  to  $C_2H_5^*$  and finally  $C_2H_6$ ; see reactions  $r_7$ ,  $r_8$ ,  $r_9$  and reverse of  $r_4$  in Table 1), and (ii) they facilitate oligomerisation reactions at lower temperatures. Therefore, optimisation of the Pd loading in these catalysts is crucial for successful coupling between the plasma and catalysis reactors, as it significantly influences the  $C_2H_4/C_2H_6$  product distribution and the formation of unwanted solid by-products.

### (c) Modelled Pd reactivity and reaction pathway analysis.

The model was applied to evaluate the forward and reverse rates of the considered reactions as a function of time and temperature, allowing for a mechanistic analysis of the catalyst reactivity. In turn, this provides insights into the reaction pathways that dictate the observed selectivity trends. The results of this analysis are presented in Fig. 5(a)–(d), highlighting the reactivity across the low- and mid-temperature regimes and high-temperature regime, respectively. Additionally, the reaction rates relevant to the following discussions are plotted in Fig. S7–S11 (ESI†) (see Section S10 of the ESI†).

Within the studied temperature range, the adsorption of both  $H_2$  (into  $2H^*$ ) and  $C_2H_2$  (into  $C_2H_2^*$ ), onto the Pd surface occurs very rapidly, with rates approaching  $10^{25} s^{-1}$ . Following the formation of  $C_2H_2^*$  and  $H^*$ , sequential surface

hydrogenation reactions ( $r_7$ ,  $r_8$  and  $r_9$  in Table 1) proceed, generating  $C_2H_3^*$ ,  $C_2H_4^*$  and  $C_2H_5^*$  species – with varying surface coverage, depending on the temperature (as shown in Fig. 5). At temperatures below  $180^\circ C$  (Fig. 5a), desorption of  $C_2H_4^*$  (reverse of reaction  $r_3$ ) is preferred, leading to the evolution of  $C_2H_4(g)$  over further hydrogenation to  $C_2H_5^*$  ( $r_9$ ). This preference results in the predominance of the desired  $C_2H_4$  product at low temperatures, aligning with the selectivity results observed in our experiments with the 0.1% Pd/ $Al_2O_3$  catalyst. The desorption of  $C_2H_4^*$  into  $C_2H_4(g)$  peaks at  $144^\circ C$ , coincide with the highest  $C_2H_4$  selectivity. In this temperature range, the coverage of C1 surface species remains negligible, as dissociative desorption of  $CH_4$  ( $r_6$ ) does not occur.

As the temperature rises, the rate of  $C_2H_4^*$  desorption decreases, whilst the rates of  $C_2H_4^*$  hydrogenation to  $C_2H_5^*$  and subsequent hydrogenation to  $C_2H_6(g)$  ( $r_4$ ) increase significantly (Fig. S7 and Fig. 5b, ESI†). This behaviour was also observed by Wang *et al.*<sup>43</sup> and Shi *et al.*<sup>44</sup> for  $C_2H_2$  hydrogenation over Cu and Au-based catalysts. As a result, the  $C_2H_6$  product sees a rise in selectivity and it becomes the main product from  $\sim 180^\circ C$ .

As the temperature is further increased, the desorption rate of  $C_2H_4^*$  falls sharply, dropping to approximately zero around  $280^\circ C$ . Simultaneously, the hydrogenation reactions to  $C_2H_5^*$



Fig. 5 Reaction pathway diagrams illustrating the reactions between the gaseous reactants ( $C_2H_2$ ,  $H_2$  and  $CH_4$ ) and the catalyst surface (a) below  $180^\circ C$ , (b) between  $180$  and  $480^\circ C$ , (c) between  $480$  and  $680^\circ C$  and (d) above  $680^\circ C$ . The resulting adsorbed surface species (marked with \*) and their reactions with other surface species are also shown. The eventual desorption of the  $C_2H_4$  (blue),  $C_2H_6$  (green) and  $CH_4$  (red) products (with varying concentrations depending on the temperature) is indicated by the cloud-shaped text boxes. Adsorption reactions are indicated by black arrows, surface hydrogenation reactions by mustard arrows, and surface dissociation reactions by orange arrows. The thickness of the arrows and the size of the blocks are qualitatively representative of the reaction rates and species surface coverage, respectively.



and  $C_2H_6(g)$  accelerate, making  $C_2H_6$  the only product seen by the model between 280 and 450 °C. These rates are plotted in Fig. S8 (ESI†). However, once the temperature reaches 450 °C, the dissociation of  $C_2H_5^*$  into  $CH_3^*$  and  $CH_2^*$  ( $r_{10}$ ) begins to occur, as shown in Fig. 5b, competing with the hydrogenation to  $C_2H_6$ . In turn, this gives rise to the production of  $CH_4(g)$ , as  $CH_3^*$  undergoes surface hydrogenation (reverse of the  $r_6$  reaction, as detailed in Fig. S9, ESI†). Thus, at temperatures above 450 °C,  $CH_4$  becomes a product of  $C_2H_2$  hydrogenation over this Pd catalyst, with its selectivity rising rapidly with temperature (cf. Fig. 4 above).

Interestingly, for all three Pd loadings, the model predicts the reappearance of  $C_2H_4$  as a product between ~500 and 710 °C, depending on the Pd loading (see Fig. 4 above), with a local maximum in  $C_2H_4$  selectivity around 600 °C. This trend is corroborated by our rate analysis, which indicates a second region of  $C_2H_4^*$  desorption into  $C_2H_4(g)$  (reverse of  $r_3$ ) within this temperature range (see Fig. S10 and Fig. 5c, ESI†). Concurrently, the dissociation rate of  $C_2H_5^*$  into  $CH_3^*$  and  $CH_2^*$  ( $r_{10}$ ) steadily rises from 500 °C, and  $C_2H_3^*$  also begins to undergo surface dissociation into  $CH_2^*$  and  $CH^*$  ( $r_{12}$ ) (see Fig. 5c). These dissociation processes explain the sharp decline in  $C_2H_6$  selectivity at elevated temperatures (cf. Fig. 4), as they compete with the hydrogenation steps required to form the  $C_2H_4$  and  $C_2H_6$  products. Indeed, the reaction rates of both  $C_2H_4^*$  and  $C_2H_5^* + H^*$  ( $r_9$  and  $r_4$ ) dwindle with increasing temperature (Fig. S10, ESI†). Besides, the observed waning  $C_2H_6$  production can also be ascribed to dissociative adsorption of  $C_2H_6(g)$  into  $2CH_3^*$  (reverse of  $r_5$ ) (cf. Fig. 5c), which becomes significant from 600 °C onwards. Collectively, these reactions contribute to enhancing the catalyst surface coverage with  $CH_x^*$  species, ultimately resulting in the evolution of  $CH_4(g)$  – which becomes the dominant product above ~650 °C.

Beyond 680 °C, additional dissociation reactions begin to take place alongside those discussed above. These are the dissociation of  $C_2H_2^*$  into  $2CH^*$  ( $r_{13}$ ),  $C_2H_4^*$  into  $2CH_2^*$  ( $r_{11}$ ) and  $C_2H_6(g)$  into  $C_2H_5^*$  and  $H^*$  (reverse of  $r_4$ ), as illustrated in Fig. 5d, with rates shown in Fig. S11 (ESI†). At the same time, all  $C_2H_y^*$  hydrogenations become slower, while the hydrogenation rates of  $CH^*$  (reverse of  $r_{15}$ ) and  $CH_2^*$  steadily increase (cf. thickness of the arrows in Fig. 5d). As a result, the formation of  $C_2$  hydrocarbons is further weakened, becoming negligible above 700 °C. Meanwhile, the  $CH_4$  production peaks, approaching 100% selectivity at 750 °C and explaining the trend in Fig. 4.

## 4. Conclusions

In this work, we developed a surface micro-kinetic model that simulates the catalytic  $C_2H_2$  hydrogenation to  $C_2H_4$ , following plasma-based non-oxidative  $CH_4$  coupling. We validated the model against experiments using an NPD plasma reactor chemically and thermally integrated with a downstream catalyst bed, employing different Pd/ $Al_2O_3$  materials with Pd loadings of 0.1%, 0.5% and 1%. All three catalysts effectively convert the  $C_2H_2$  present in the exiting gas stream from the plasma discharge

without external heating, with conversions above 90%. By applying fixed plasma conditions, we attain a consistent  $CH_4$  conversion around 46%, and  $C_2H_2$  selectivity around 83% for the plasma stage, and thus post-plasma catalytic  $C_2H_2$  hydrogenation into  $C_2H_4$  is the main driver of the final  $C_2H_4$  yield. Our experiments show that only the 0.1% Pd/ $Al_2O_3$  catalyst evolves  $C_2H_4$  as the main hydrogenation product, while at higher Pd loadings,  $C_2H_6$  is predominantly produced. Our model predicts a slightly different trend, with higher  $C_2H_4$  selectivity for all catalysts in the low-temperature regime, though  $C_2H_6$  rapidly becomes predominant above 150–180 °C. The highest  $C_2H_4$  selectivity is obtained at the lowest simulated temperature (*i.e.*, 142 °C, 135 °C and 115 °C for the 0.1%, 0.5% and 1% Pd/ $Al_2O_3$  catalysts, respectively). In the experiments, other oligomerisation by-products are also observed, but they are not included in the model, which might explain the observed discrepancy.

Our results also show that the exothermic nature of the hydrogenation reactions induces a temperature rise within the catalyst bed, which is detrimental to the  $C_2H_4$  selectivity. This is in line with the modelled reaction mechanism, which reveals that by increasing the catalyst temperature, the  $C_2H_4^*$  desorption rate is lowered, while further hydrogenation is favoured. As this effect is highly undesirable, the deployment of more selective catalysts (*e.g.*, mixed metal alloys)<sup>45,46</sup> able to fine-tune these rates may enhance the process performance.

Other key factors may influence the coupling between the plasma reactor and the catalyst bed. We believe these include the type of catalyst and support (*i.e.*, oxides *versus* metal-based), the plasma source, reactor geometry, the magnitude and type of gas flow, type of filter, and the distance between the bed and discharge region. Ultimately, these factors directly impact heat transfer, and in turn the catalyst temperature, which, as shown in this work, significantly affects the selective synthesis of  $C_2H_4$ . Tailoring these variables allows for fine control over the catalyst bed temperature, thereby maximising  $C_2H_4$  selectivity (and yield) and catalyst performance. This research opens avenues for further exploration of coupling different plasma sources and reactors with simple post-plasma catalytic setups. Potentially, the flexibility in adjusting the catalyst bed temperature through the aforementioned factors may allow for the use of cheaper and more abundant catalysts (such as Cu and Ni), which generally require higher activation temperatures.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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