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Short communication

Hybrid plasma catalysis-thermal system for non-oxidative coupling of methane to ethylene and hydrogen

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ABSTRACT

We report a two-stage hybrid plasma catalysis-thermal system for non-oxidative coupling of methane (NOCM) to ethylene (C₂H₄) and hydrogen (H₂), achieving 66 % C₂H₄ selectivity and 60 % H₂ selectivity with 28 % CH₄ conversion. This corresponds to a C_2H_4 yield of 18 %, which is one of the highest reported in literature. The system consists of the first plasma catalysis stage (stage 1) and the second thermal cracking stage (stage 2). Comprehensive analyses using in-situ mass spectrometry (MS) and gas chromatography (GC) reveal that the combination of plasma and Pt/ZrO2 catalyst in stage 1 predominantly facilitates the conversion of methane to ethane. Characterizations employing X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy-scanning transmission electron microscopy-energy dispersive X-ray (HRTEM-STEM-EDX) mapping, and hydrogen temperature-programmed reduction (H2-TPR), indicate that the coordinatively unsaturated site of Pt could be the active sites for C-H bond cracking to generate abundant CH₃ radicals (CH₃·), enhancing the C₂ selectivity by inhibiting the non-selective formation of coke and higher hydrocarbons. Subsequently, the products from stage 1 (especially C₂H₆) undergo pyrolysis reactions at 880 °C in stage 2, which further boosts the C₂H₄ selectivity and yield. Based on the reaction performance, catalyst characterization, optical emission spectroscopy (OES), and in-situ Fourier transform infrared spectroscopy (FTIR) results, we reveal the reaction mechanism within the hybrid two-stage plasma catalysis-thermal system for converting CH_4 to C_2H_4 and H₂.

1. Introduction

Methane (CH₄), being the least reactive hydrocarbon, presents a significant challenge for conversion into other products due to its robust C–H bond strength (439 kJ mol⁻¹), [1,2] high ionization potential (12.6 eV), [3] low acidity, minimal proton affinity (-1.9 eV), [4] and low polarizability (2.8×10^{-40} C² m² J⁻¹). [5] This resistance stems from the CH₄ inherent chemical properties, making its transformation particularly arduous. The direct conversion of CH₄ to value-added ethylene (C₂H₄) has predominantly been explored through two methodologies, i. e., oxidative coupling of methane (OCM) and non-oxidative coupling of methane (NOCM). OCM is effective in achieving high CH₄ conversion, but it suffers from the drawback of producing undesired CO₂, thereby

diminishing the selectivity of C_2H_4 . [6–9].

NOCM has attracted increasing attention in recent years, [10–12] for avoiding the production of CO₂. Šot et al., have shown material-induced NOCM to higher hydrocarbons (C₂H₆, C₂H₄, C₂H₂, C₆H₆) with 20 % selectivity, but only 3 % CH₄ conversion at 1080 °C. [13] Furthermore, Guo et al. reported up to 48 % CH₄ conversion at a slightly higher temperature of 1090 °C. [14] Additionally, catalysts, such as In/SiO₂, [15] Mo₂C[B]ZSM-5, [16] Fe-Mo/HZSM, [17] and GaN/SBA15, [18] have been examined for NOCM, achieving no more than 2 % CH₄ conversion at temperatures below 1000 °C. Aside from transition metals featuring partially coordinately unsaturated metal centers, [19–23] studies have predominantly focused on Pt-containing catalysts. Earlier investigations into CH₄ activation demonstrated that a 6 % Pt/SiO₂

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Received 20 June 2024; Received in revised form 19 August 2024; Accepted 11 September 2024 Available online 16 September 2024 1385-8947/© 2024 Published by Elsevier B.V. catalyst facilitated the formation of higher hydrocarbons. [24] Notably, Pt/HX and Pt/HY catalysts have been employed in NOCM, showing improved CH₄ conversion and enhanced product selectivity towards C₃ and C₅ compounds. [25] Chen et al. highlighted that incorporating Pt into Mo-HZSM-5 significantly boosts the catalytic performance by reducing coke formation. [26] Moreover, Gerceker and colleagues found that Pt-Sn zeolites exhibit high selectivity towards C₂H₄ (up to 90 %) albeit with low CH₄ conversion (<0.3 %). [27] Xiao and Varma developed a 1 % Pt-Bi/HZSM-5 catalyst, demonstrating over 90 % selectivity to C₂H₆ and 2 % CH₄ conversion. [28] Moreover, Pt/CeO₂ catalysts have been thoroughly investigated in NOCM through experimental and theoretical studies. [29-33] Pt-based catalysts have been extensively studied and have been shown to be effective in producing C₂H₆ in the NOCM reaction. Although their high cost, Pt-based catalysts remain the best option for CH₄ conversion to C₂H₆. In addition, Pt-based catalysts with a very low loading can achieve high alkane selectivity. Despite these advances, significant challenges persist, particularly the high operational costs and catalyst deactivation caused by coke deposition and sintering. These issues are largely due to the need for high temperatures to achieve substantial conversions.

In the context of CH₄ conversion reactions, non-thermal plasma primarily converts CH_4 into C_2H_6 , while thermal plasma primarily produces C₂H₂. According to the thermodynamic equilibrium calculations for CH₄, C₂H₄ formation occurs at around 900 °C. However, the conversion of CH₄ through standalone thermal cracking is very low. To address thermodynamic limitations, in our previous work, a two-stage plasma-catalysis thermal cracking system can simultaneously achieve both high CH₄ conversion and high C₂H₄ selectivity. [34] The process begins with CH₄ activation in a dielectric barrier discharge (DBD) plasma stage at a mild temperature, followed by the dehydrogenation of alkanes to C₂H₄ in a thermal cracking stage. However, the yield of C₂H₄ remains unsatisfactory. Kawi et al. [35] reported on the use of a Pt/CeO2 catalyst with DBD plasma for NOCM, which facilitates the dissociation of CH₄ C-H bonds at low temperatures. They achieved a CH₄ conversion of 39 % and a C₂ selectivity of 54 % at 54 W. Similarly, Song et al. [36,37] investigated a Pt/Al₂O₃ catalyst for the conversion of CH₄ to higher hydrocarbons using DBD plasma, with the major products being alkanes such as C₂H₆ and C₃H₈. As mentioned above, Pt-based catalysts are capable of not only activating CH₄ but also demonstrating high selectivity towards alkanes. Non-thermal plasma with catalysts can also convert CH₄ to C₂H₄, but the yield of C₂H₄ is relatively low and does not meet industrial requirements. [38] Currently, there are three main technologies for NOCM to produce C₂H₄: non-thermal plasma catalysis, thermal plasma catalysis, and thermal catalysis. Compared to nonthermal plasma catalysis, the two-stage system offers a higher C₂H₄

yield. In comparison with thermal plasma catalysis, the two-stage system has lower coke selectivity, operates more stably, and is more advantageous for industrial applications. Additionally, compared to thermal catalysis, the two-stage system achieves a higher C₂H₄ yield at a lower temperature, making it more suitable for practical industrial.

In the present paper, we investigated the NOCM using Pt/ZrO_2 catalyst by a two-stage hybrid plasma catalysis-thermal system (Scheme 1). Hence, the novelty with our previous work is the introduction of a catalyst in the plasma setup. Our results indicate that the Pt/ZrO_2 catalyst enhances both the dissociation of CH_4 and the C–C coupling reactions, culminating in a notable C_2H_6 selectivity of 62 %. Subsequently, we achieved 66 % C_2H_4 selectivity and 28 % CH_4 conversion after the thermal cracking stage at 880 °C, alongside 61 % H_2 selectivity. The experimental details, including experimental setup, catalyst preparation, and catalytic tests, are shown in Supporting Information (SI).

2. Results and discussion

2.1. Catalytic performance

We developed a two-stage hybrid plasma catalysis-thermal system for the direct conversion of CH_4 to C_2H_4 and H_2 , as depicted in Figure S1. To evaluate the efficiency of the NOCM reaction over a Pt/ZrO₂ catalyst via a two stage tandem process and to ascertain the functionality of each stage, four distinct experimental setups were employed, including plasma alone (stage 1), plasma + Pt/ZrO₂ (plasma with Pt/ZrO₂ catalyst packing in stage 1), plasma alone + T (plasma alone in stage 1, followed by thermal cracking in stage 2), and plasma + $Pt/ZrO_2 + T$ (plasma with Pt/ZrO₂ catalyst packing in stage 1, followed by thermal cracking in stage 2), as illustrated in Fig. 1(A-D). Different Pt loadings (Table S1 and S2) and different supports (Table S3) have been investigated in the plasma stage, as shown in Figure S2 and Figure S3, and the corresponding discussion can be found in the Supporting Information. The optimal C₂H₆ yield was achieved with 0.5 %Pt/ZrO₂ catalyst in NOCM. Because ZrO₂ can anchor Pt, which is beneficial for Pt dispersion and CH₄ dissociation at Pt sites, further enhancing CH₄ conversion. Moreover, the feed gas ratio in plasma + Pt/ZrO₂ system was investigated in Figure S4.

In the plasma alone system (Fig. 1A), the CH₄ conversion reaches 26.6 %, with C_2H_6 being the predominant hydrocarbon product at 43.0 % selectivity, and the selectivity of C_2H_4 is only 3.6 %. A notable enhancement in C_2H_6 selectivity to 61.9 %, along with a significant reduction in propane (C_3H_8) and coke selectivity, is observed in Fig. 1B upon introducing 0.5 % Pt/ZrO₂ catalyst, indicating that the Pt/ZrO₂ catalyst improves C_2H_6 formation and inhibits coke formation.



Scheme 1. Scheme 1. Hybrid plasma Catalysis-Thermal System for Non-oxidative Coupling of Methane to Ethylene and Hydrogen.



Fig. 1. (A-D) Product distribution and CH₄ conversion across various reaction systems, which was repeated five times. Error bars represent the standard deviation of the measurements: (A) plasma alone, (B) plasma + Pt/ZrO_2 , (C) plasma alone + T, (D) plasma + Pt/ZrO_2 + T; (E-F) Comparative analysis of NOCM reaction performance in plasma alone and plasma + Pt/ZrO_2 system: (E) Temporal evolution of MS signal intensities and (F) gas chromatography profiles; (G) Comparison of this study with some representative results from literature for NOCM (with diamond, star and triangle symbols for thermal, non-thermal plasma, and thermal-plasma catalysis, respectively). The numbers given next to the symbols correspond to the references in this paper; more information about the conditions for these references can be found in Table S4 (0.5 wt% Pt loading; T represents thermal cracking temperature is 880 °C).

Furthermore, compared to other Pt-based catalysts, the 0.5 %Pt/ZrO2 catalyst shows a higher CH₄ conversion (29.1 %), suggesting its better efficacy in CH₄ dissociation. Compared with plasma alone (Fig. 1A), in Fig. 1C, the C_2H_6 selectivity decreases from 43.0 % to 6.5 %, while the C₂H₄ selectivity increases from 3.6 % to 60.1 %, along with 22.5 % CH₄ conversion, demonstrating the hybrid plasma-thermal system enhances C₂H₄ generation. The C₂H₄ yield of 13.5 % surpasses our previous result of 10.7 %. [34] As shown in Fig. 1D, incorporating the Pt/ZrO₂ catalyst in stage 1 results in a higher CH₄ conversion (27.6 %) and C₂H₄ selectivity (65.9%). However, the H₂ selectivity slightly decreases from 62.4 % (Fig. 1C) to 60.5 % (Fig. 1D). The yields of C_2H_4 and H_2 reach 18.2 % and 16.7 % (Table S5), respectively. The effect of discharge voltages in stage 1 and thermal cracking temperature in stage 2 on NOCM performances have been investigated (Figure S5), which indicates that high discharge voltage favors CH₄ conversion and thermal cracking at high temperature (880 °C) facilitates C2H4 selectivity. Furthermore, thermodynamic equilibrium calculations demonstrate that the most favorable range of temperature for C₂H₄ generation is 680–1080 °C, excluding production of solid carbon and C₆H₆ (Figure S6-S8).

Compared to the plasma alone system and the plasma $+ Pt/ZrO_2$ system, the H₂ selectivity increases from 49.1 % to 62.4 % and from 42.1 % to 60.5 % in the plasma + T and plasma + Pt/ZrO_2+T systems, respectively, as shown in Table S5. Since C₂H₆ contains 6 hydrogen atoms, while C₂H₄ contains only 4 hydrogen atoms, the selectivity for C_2H_6 decreases and the selectivity for C_2H_4 increases in the plasma + T and plasma + Pt/ZrO_2+T systems. This results in the release of more H atoms, leading to a higher production of H₂. Conversely, compared to the plasma alone system, the selectivity for C₂H₆ increases in the plasma + Pt/ZrO₂ system, which results in a lower H₂ selectivity. The carbon balance of the NOCM reaction under the optimized $plasma + Pt/ZrO_2$ reaction conditions has been verified to be ca. 92.6 % (Figure S9). The SEM images of coke for both the plasma alone system and the plasma + T system are shown in Figure S10. Usually, in plasma alone system for NOCM reaction, with increasing the CH₄ conversion, the C₂ selectivity decreases, and the coke selectivity increases, which belong to a gas phase reaction. However, in the plasma + Pt/ZrO2 system for NOCM reaction, the C₂ selectivity increases with increasing the CH₄ conversion and the decreasing of the coke, which indicates that Pt/ZrO2 catalyst plays an important role in promoting surface reactions, accelerating CH₄ conversion to produce C₂H₆. In summary, introducing a Pt/ZrO₂ catalyst in the plasma (stage 1) favors CH₄ conversion to C₂H₆. 12 h continuous tests for the NOCM reaction in both "plasma alone + T" and "plasma + $Pt/ZrO_2 + T$ " systems, as shown in Figure S11, further indicate that the "plasma + Pt/ZrO₂ + T" system more effectively dissociates CH₄, thereby improving the C₂H₄ yield.

Fig. 1E illustrates the temporal profiles of various m/z signals detected through mass spectrometry (MS), representing different chemical species observed during the experiments of "plasma alone" and "plasma + Pt/ZrO₂". To meticulously capture the evolution of reaction products, both reaction systems were continuously operated without interruption. Initially, NOCM was conducted in a DBD reactor, transitioning from plasma-on to plasma-off mode for a duration of 60 mins to characterize the "plasma alone" system. Following a quiescent period of approximately 130 mins with the discharge turned off, the experiment was resumed under the "plasma + Pt/ZrO₂" configuration for another 60 mins. Notably, the transition from "plasma alone" to "plasma + Pt/ZrO₂" manifests in a reduced intensity of the m/z = 2 signal (corresponding to H₂), while the intensity of m/z = 30 (exclusively attributed to C₂H₆) substantially increases. This observation strongly supports the hypothesis that the Pt/ZrO₂ catalyst favors the formation of C₂H₆.

Moreover, the MS profiles further reveal a decline in C_3H_8 in the "plasma + Pt/ZrO₂" system compared to the "plasma alone" system. This suggests an increased demand for H atoms due to the enhanced selectivity towards C_2H_6 , leading to a reduced availability of isolated H atoms in the discharge gas. Consequently, the H₂ selectivity decreases. The preferential consumption of CH₃· for C–C coupling to produce C_2H_6

implies a reduction in coke formation, owing to insufficient CH₃· availability for gradual dehydrogenation (CH₃· \rightarrow CH₂· \rightarrow CH· \rightarrow C). Furthermore, the formation of C₃ adsorbates might be impeded due to the limited utilization of CH₃· for combining with C₂H₅·, thus hindering the formation of C₃H₈ (CH₃· + C₂H₅· \rightarrow C₃H₈). These findings align with the reaction behavior depicted in Fig. 1A and 1B, reinforcing the catalysis of Pt/ZrO₂ in regulating the product distribution to generate more C₂H₆.

The gas chromatogram (GC) profiles, depicting the product distributions for both the "plasma alone" and the "plasma + Pt/ZrO₂" systems are illustrated in Fig. 1F and Figure S12. It can be seen that the predominant products in the "plasma alone" system are C₂H₆ and C₃H₈. The formation of C₂H₆ indicates H abstraction from two CH₄ molecules, resulting in the formation of two CH₃· radicals, which subsequently undergo C–C coupling $(CH_3 + CH_3 \rightarrow C_2H_6)$. [39] Additionally, the formation of C₃H₈ is attributed to the combination of a CH₃· radical with an C₂H₅· radical (CH_3 · + C_2H_5 · \rightarrow C_3H_8). [39] A comparison between the "plasma alone" system and the "plasma + Pt/ZrO₂" system reveals an increase in the intensity of C₂H₆ and a decrease in C₃H₈, aligning well with the observations noted in Fig. 1E. Since a significant portion of CH₃. is used for coupling to form C₂H₆, the amount of CH₃· available for C₃H₈ reduced, leading to a decrease in C₃H₈ production. C₂H₅, primarily come from the dissociation of C₂H₆. As the amount of stable C₂H₆ increases, the amount of C₂H₆ undergoing dissociation decreases, resulting in a reduction in the production of C2H5. and consequently a decrease in C₄H₁₀. The GC profiles of the other systems have also been thoroughly investigated and are presented in Figure S13.

In Fig. 1G, remarkably, the yield of C_2H_4 in this study surpasses the values reported in most of the existing literature, including both thermal catalysis (refs 16–18, 27, 40, 41) and plasma catalysis (refs 34, 35, 42–44) [16–18,27,34,35,40–44] (indicated by diamonds and stars in Fig. 1G, respectively). It is however a little lower than the value observed in one paper. [41] On the other hand, the operational temperature of 880 °C in our research is significantly lower than the 1090 °C used in that reference, [41] thereby improving the practicality of this hybrid plasma catalysis-thermal system. Moreover, the yield of C_2H_4 in the NOCM reaction of nanosecond pulsed plasma (triangles in Fig. 1G) is significantly higher than in our study, and the energy cost is much lower (Table S6) [45,46]. However, the feed gas flow rate is 200 sccm, which is 10 times that of our reaction. Additionally, the reaction takes place under high pressure (5 bar), and the reactor design is complex, which may not be conducive to industrial applications.

2.2. Catalyst characterization

Fig. 2A depicts the X-ray diffraction (XRD) patterns for ZrO₂ and Pt/ ZrO₂ catalysts. Notable diffraction peaks at 20 values of 30.12, 34.96, 50.22, 59.74, 62.68, and 73.94 correspond to tetragonal ZrO₂ crystal (PDF#49-1642), with additional peaks at 28.17 and 31.47 corresponding to the monoclinic ZrO₂ crystal (PDF#37-1484). However, the XRD patterns of the Pt/ZrO₂ catalysts show no discernible diffraction peaks attributed to Pt species, which suggests a high dispersion of Pt species across the catalyst surface. High-resolution transmission electron microscopy (HRTEM) images of the Pt/ZrO2 catalyst, as illustrated in Fig. 2B, reveal distinct (-111) and (200) lattice fringes. These fringes correspond to inter-planar spacing of 0.316 nm for ZrO₂ and 0.196 nm for Pt, indicating the precise structural composition of the Pt/ZrO₂ catalyst. Fig. 2(C-F) show the HAADF-STEM-EDX mapping images of the Pt/ZrO₂ catalyst, and it can be observed that Pt and Zr are dispersed uniformly with no obvious aggregation of Pt. Such a uniform distribution of Pt species likely minimizes the formation of heavy carbonaceous species, thereby improving the selectivity towards C₂ hydrocarbons. [35] Although there is no significant Pt aggregation observed in fresh and spent 0.5 %Pt/ZrO₂ catalyst, as shown in Figure S14. TGA results analysis in Figure S9A indicates that carbon deposition has occurred on the catalyst post-reaction. This is further confirmed by XPS analysis



Fig. 2. Characterization of Pt/ZrO₂ catalyst (0.5 wt% Pt loading). (A) XRD patterns comparing ZrO₂ with Pt/ZrO₂ catalysts (both fresh and spent), (B) HRTEM images, and (C-F) HAADF-STEM-EDX element-mapping analyses of Pt/ZrO₂ catalyst. (G-I) XPS spectra of (G) Pt 4f, (H) Zr 3d, (I) O1s (The Binding Energy was calibrated by C1s at 284.8 eV), and (J) H₂-TPR profiles.

(Figure S15) and the N_2 physisorption (Table S7), which shows evidence of carbon formation, in consistent with the results in Figure S10.

Fig. 2(G-I) present the X-ray photo-electron (XPS) spectra for the Pt/ ZrO₂-Fresh and Pt/ZrO₂-Spent catalysts. In Fig. 2G, the peaks observed at binding energy of 71.3 eV and 75.3 eV are associated with Pt $4f^{7/2}$ and Pt $4f^{5/2}$ of the Pt⁰ species, [47,48] respectively. The peaks at 73.2 eV and 76.0 eV correspond to Pt $4f^{7/2}$ and Pt $4f^{5/2}$ of the Pt²⁺ species. [47,49] Additionally, signals at 74.0 eV and 78.8 eV are attributed to Pt $4f^{7/2}$ and Pt 4f^{5/2} of the Pt⁴⁺ species, [47,49] respectively. The proportion of Pt⁰, Pt²⁺, and Pt⁴⁺ species can be determined from the fitting of the XPS peak areas, as shown in Table S8. Predominantly, the Pt species in the Pt/ ZrO₂-Fresh catalyst exist in oxidized states, with only a minor fraction (18 %) of metallic Pt^0 . This fraction increases to 50.5 % in the Pt/ZrO_2 -Spent catalyst. Additionally, the contents of Pt²⁺ and Pt⁴⁺ decrease from 53.7 % and 28.3 % in the Pt/ZrO_2 -Fresh catalyst to 43.0 % and 6.5 % in the Pt/ZrO_2 -Spent catalyst, respectively. The variations in the quantities of metallic Pt⁰, Pt²⁺, and Pt⁴⁺ between the fresh and spent catalysts suggest that CH₄ plasma facilitates the reduction of PtO_x to Pt⁰. The Zr 3d spectra reveal surface compositions of Zr^{4+} and Zr^{3+} , depicted in Fig. 2H. The peaks at 182.1 eV and 184.5 eV are attributed to Zr 3d^{5/2} and $\operatorname{Zr} 3d^{3/2}$ of Zr^{4+} species, [48] while the peaks at 181.3 eV and 184.0 eV correspond to Zr $3d^{5/2}$ and Zr $3d^{3/2}$ of Zr³⁺ species. [48] The Pt/

 ZrO_2 -Spent catalyst exhibits a slightly higher (2.8 %) Zr^{3+} ratio compared to the Pt/ZrO2-Fresh (Table S5), indicating that ZrO2 is relatively stable. Furthermore, the performance of the "plasma $+ ZrO_2$ " system is nearly the same as that of the "plasma alone" system (Figure S16), suggesting that the ZrO_2 support is not a catalytically active site for the generation of C₂H₆. Thus, it can be inferred that Pt species act as the primary active sites, significantly increasing the selectivity towards C₂H₆. The O 1 s spectra reveal the presence of adsorbed oxygen (Oad, at 531.5 eV) and lattice oxygen (Olatt, at 529.9 eV) as depicted in Fig. 2I. The proportions of O_{ad} are 24.6 % and 31.7 % for Pt/ZrO2-Fresh and Pt/ZrO2-Spent, respectively, indicating the formation of oxygen vacancies (Ov) during the NOCM reaction, which is consistent with the partial reduction of Zr^{4+} to Zr^{3+} . [49] This suggests the enhanced O_v formation post CH₄ plasma treatment, facilitating the anchoring of metallic Pt and consequently augmenting the stability of the Pt/ZrO₂ catalyst.

Fig. 2J illustrates the H₂ consumption rates on ZrO₂, Pt/ZrO₂-Fresh, and Pt/ZrO₂-Spent under atmospheric pressure. H₂ is consumed below 600 °C through interactions with the surfaces of ZrO₂ (or Pt/ZrO₂), while consumption above 600 °C results from H₂ reactions with the bulk ZrO₂. [50] The reduction temperature for Pt/ZrO₂-Spent samples (227 °C and 342 °C) is marginally lower than for Pt/ZrO₂-Fresh (236 °C

and 350 °C), which is attributed to higher H₂ dissociation on metallic Pt sites or the emergence of crystal defects on the Pt/ZrO₂ surface due to CH₄ plasma exposure. Furthermore, compared with the Pt/ZrO₂-Fresh catalyst, the observed shift to lower temperatures (236 °C to 227 °C) suggests greater dispersion and smaller particles of Pt in the Pt/ZrO₂-Spent catalyst, [51] corroborated by the higher content of metallic Pt⁰ in Pt/ZrO₂-Spent (50.5 %) compared to Pt/ZrO₂-Fresh (18.0 %), as shown in Fig. 2G. These findings underscore the role of highly dispersed Pt as active sites, not only in facilitating C–C coupling towards the preferential formation of C₂H₆ but also in minimizing carbon coking. [35].

3. Discussion of reaction mechanisms

The Current-Voltage characteristics and Lissajous figures for both the plasma alone system and the plasma + Pt/ZrO₂ catalyst system are illustrated in Fig. 3. As depicted in Fig. 3A, with constant input voltage, the effective voltage in the plasma + Pt/ZrO_2 system (11.5 kV) is higher than that in the plasma alone system (10.3 kV), as well as the microdischarge currents. This difference leads to a greater effective power (P) in the case of plasma + Pt/ZrO_2 (27.6 W) compared to the plasma alone system (25.6 W), which were calculated by Lissajous plots area S $(P = f \times C_m \times S)$, as demonstrated in Fig. 3B. Fig. 3C and 3D illustrate the in-situ optical emission spectra (OES) of the CH₄/Ar plasma. The lines at 314 nm and 430 nm are assigned to CH species corresponding to $C^{2}\Sigma^{+} \rightarrow X^{2}\Pi$ and $A^{2}\Delta \rightarrow X^{2}\Pi$ transitions, respectively. [52] CH· species usually originates from the stepwise dehydrogenation of CH3. produced by the dissociation of CH₄. This indicates the presence of CH₃·, CH₂· and CH species in the CH₄/Ar plasma. Besides the hydrocarbon radicals, transitions of excited hydrogen-related species, such as H_y (434 nm), as well as excited Ar atoms (690-970 nm), are also detected. [53,54] The N₂ second positive system (337 nm, 358 nm, and 381 nm) and the first negative band (391 nm) observed in the spectra can be attributed to micro-discharges of air occurring at the external grounding electrode, as shown in Figure S17. Moreover, the electron density in atmosphericpressure low-temperature discharges was measured by the line-ratio method of OES, [55] the electron density of plasma + Pt/ZrO2 is higher than that of plasma alone, as shown in Table S9. This indicates that catalyst packing is more conducive to CH₄ conversion. In summary,

compared to a plasma alone system, the DBD plasma reactor with Pt/ ZrO₂ packing increases the effective voltage and electron density, enhancing the discharge and thereby improving CH₄ conversion. The electron energy distribution function (EEDF) was show in Figure S18, which indicates that the proportion of electrons with lower energies decreases when Pt/ZrO₂ is present in the plasma reactor. Additionally, the range of the EEDF broadens in plasma + Pt/ZrO₂ system, signifying that more electrons with higher energies are generated in the DBD plasma.

To further elucidate the reaction mechanisms, in-situ Fourier transform infrared (FTIR) spectroscopy was employed to investigate the evolution of species during NOCM in both the "plasma alone" and "plasma + Pt/ZrO2" systems, employing a self-designed in-situ FTIR cell (Figure S19). In Fig. 4A, it is evident that there are deformation vibration peaks of the C–H bonds in CH_3^* at 1380 cm⁻¹ and 1465 cm⁻¹, a symmetrical stretching vibration peak of the C-H bonds in CH₃* at 2870 cm⁻¹, and an asymmetric stretching vibration peak of the C–H bonds in CH_3^* at 2970 cm⁻¹. These results indicate the presence of a significant amount of CH₃, radical species in the CH₄/Ar plasma for the NOCM using the "plasma alone" system, confirming that C₂H₆ is mainly produced from the coupling of CH₃, which is consistent with experimental and simulation results. [56-58] In Fig. 4B, the NOCM in the "plasma + Pt/ZrO2" system also exhibits distinct C-H vibration peaks of CH3* species, including the deformation vibration peaks at 1380 cm⁻¹ and 1465 cm⁻¹, the symmetrical stretching vibration peak of the C–H bonds in CH₃* at 2870 cm⁻¹, and the asymmetric stretching vibration peak of the C–H bonds in CH_3^* at 2965 cm⁻¹. The peak at 1595 cm⁻¹ can be attributed to the C=C skeletal vibration of aromatic carbon, and such carbon deposits may be formed from carbonaceous materials, such as the aromatic structures found in graphite or carbon black. [59] Obviously, the intensity of the carbon deposition peak in plasma alone system is lower than that in plasma + Pt/ZrO₂ system, because plasma alone system for NOCM reaction belongs to gas phase, and the coke is adhered to the reactor wall, while in the plasma + Pt/ZrO₂ system, the coke deposited on the catalyst surface and the peak intensity enhanced with time on stream. The time to reach a steady state differs between the plasma alone system and the plasma + Pt/ZrO₂ system. The plasma alone system, which involves only gas-phase reactions, quickly reaches a



Fig. 3. Comparative analysis of discharge parameters: (A) Waveforms of discharge voltage and discharge currents; (B) Lissajous plots. (C) and (D) Typical optical emission spectra for plasma alone versus plasma + Pt/ZrO_2 system.

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thermal cracking routes: $----- C_2H_6$ $----- C_3H_8$ $------ C_4H_{10}$ $---- C_2H_6C_3H_8C_4H_{10}$

Fig. 4. In-situ FTIR spectra: (C) plasma alone system and (D) plasma + Pt/ZrO_2 system. (E) Schematic representation of the reaction mechanisms within the hybrid two-stage plasma catalysis-thermal system for NOCM to C_2H_4 and H_2 .

steady state. Consequently, the intensities of CH₃ and carbon species stabilize rapidly. In contrast, the plasma + Pt/ZrO₂ system includes both gas-phase and surface reactions. Characterization results indicate that Pt serves as the active site for NOCM. During the reaction, PtO is gradually reduced to form Pt, facilitating CH₄ dissociation and C–C coupling on the catalyst surface, which has been confirmed by Figure S20. As a result, the time to reach a steady state is longer in plasma + Pt/ZrO₂ system, and the intensities of CH₃ and carbon species increase gradually as the reaction progresses. This further demonstrates that metallic Pt sites are more favorable for activating and dissociating CH₄, thereby adsorbing more CH₃* and leading to the production of more C₂H₆. Compared to the plasma alone system, the stretching vibration peak of the C–H bonds shifts to a lower wavenumber at 2965 cm⁻¹, which is speculated to be caused by chemisorption of CH₃* on metallic Pt sites.

Based on the *in-situ* diagnostics and evaluation of the reaction performance, we propose a plausible reaction mechanism in Fig. 4C for the hybrid plasma catalysis-thermal system to produce C_2H_4 and H_2 through the NOCM route. The role of Stage 1 is to convert CH_4 into C_2H_6 . In the case of "plasma alone", the primary reaction involves plasma activation of CH_4 to generate CH_x species (dominated by CH_3 ·), which then react with each other through C–C coupling to form C_2H_6 in the plasma. [60] In the case of the "plasma + Pt/ZrO₂" system, in addition to the previously mentioned C–C coupling in the gas phase, C_2H_6 is generated more easily in the "plasma + Pt/ZrO₂" system through two distinct pathways. Path 1: the plasma directly activates CH_4 in the discharge zone to form C_3H_6 through surface C–C coupling. Path 2: CH_4 molecules first adsorb on the active Pt sites, and then energetic species (electrons and radicals) generated by the plasma react with adsorbed CH_4 to form adsorbed H and CH_3^* species (O), which finally produce C_2H_6 through surface C–C coupling (O). Then, Pt/ZrO₂ is used again to adsorb CH_4 molecules (O).

The coordinatively unsaturated Pt sites are more active for C–H bond scission and metallic Pt atoms can improve the C_2 selectivity by hindering the formation of coke and higher hydrocarbons. [29,35] It can be

inferred that electrons from Pt are transferred to the C-H anti-bonding orbital of CH₄, leading to weakening of the C-H bond and lowering of the barrier for C-H bond dissociation, thereby facilitating CH₄ cracking to produce CH₃· species. [61] The robust electron circulation capability of Pt allows it to donate a portion of d orbital electrons to the antibonding orbital of CH₃·, while concurrently receiving electrons from CH_3 · into its vacant d orbitals. This reciprocal electron transfer modulates the electron density of CH₃, diminishing their reaction energy barrier and thus simplifying C-C coupling on the Pt site. [57] Following the desorption of C₂H₆, the Pt site is poised to adsorb CH₄ or CH₃· again (③), fostering further CH_4 cracking (①) and C_2H_6 production (②). Moreover, compared to the "plasma alone" system, the "plasma + Pt/ ZrO2" system exhibits reduced selectivity for C3H8 and coke formation, attributed to the preferential coupling of CH3. to form C2H6 over its gradual dehydrogenation to carbon or coupling with C₂H₅. to generate C₃H₈. However, some C₂H₆ undergoes dehydrogenation or collides with high-energy electrons to form C2H5, which then couples with CH3 or C_2H_5 · to produce C_3H_8 and C_4H_{10} in Stage 1 of the plasma + Pt/ZrO₂ system.

In Stage 2, the focus shifts to the thermal cracking of alkanes into $C_{2}H_{4}$, primarily by $C_{2}H_{6}$ thermal cracking, since $C_{2}H_{6}$ is the main product of Stage 1. In addition, C₂H₆ cracking achieves the highest ethylene yield among the C2-C4 alkane cracking reactions, as shown in Figure S21. The thermal cracking process is initiated by the generation of CH₃· radicals, which, through chain propagation, interact with C₂H₆ to produce C_2H_5 radicals $(CH_3 + C_2H_6 \rightarrow C_2H_5 + CH_4)$. [62] These radicals further decompose to yield C₂H₄ and H· radicals, $(C_2H_5 \rightarrow C_2H_4 + H)$, with the latter coupling with C_2H_6 to form H_2 ($H \rightarrow H_2$) $C_2H_6 \rightarrow C_2H_5 + H_2$). [59,63] The main pathways for C₂H₄ production from C₃H₈ thermal cracking are as follows [64,65]: C₃H₈ cracks to produce C_2H_5 and CH_3 ($C_3H_8 \rightarrow C_2H_5 + CH_3$), where C_2H_5 can directly decompose to C_2H_4 and $H \cdot (C_2H_5 \rightarrow C_2H_4 + H \cdot)$ or react with C_3H_8 to form C_2H_6 and C_3H_7 ($C_2H_5 + C_3H_8 \rightarrow C_2H_6 + C_3H_7$). C_3H_7 can also be formed by H· radicals reacting with C_3H_8 (H·+ $C_3H_8 \rightarrow H_2$ + C_3H_7 .). The C_3H_7 . then decomposes to yield C_2H_4 and CH_3 . $(C_3H_7 \rightarrow C_2H_4 + CH_3)$, with the latter reacting with C_3H_8 again to produce C_3H_7 and CH_4 ($CH_3 + C_3H_8 \rightarrow CH_4 + C_3H_7$). Although C_4H_{10} production in Stage 1 is minimal, it still contributes to C₂H₄ formation. C₄H₁₀ cracking follows two pathways [66-68]: the first involves cracking to form C_2H_5 · ($C_4H_{10} \rightarrow C_2H_5 \cdot + C_2H_5 \cdot$), which then decomposes to C₂H₄ and H₂, or reacts with C₄H₁₀ to form C₄H₉ ($C_2H_5 + C_4H_{10} \rightarrow$ $C_2H_6 + C_4H_9$), which subsequently decomposes again to yield C_2H_5 . and C_2H_4 ($C_4H_9 \rightarrow C_2H_4 + C_2H_5 \rightarrow$). The second pathway involves C_4H_{10} cracking to produce CH₃· and C₃H₇· ($C_4H_{10} \rightarrow CH_3 + C_3H_7$ ·), with C₃H₇· decomposing to form C₂H₄ and CH₃, and the CH₃ then reacting with C_4H_{10} to form C_4H_{9} and CH_4 (CH_3 + $C_4H_{10} \rightarrow CH_4 + C_4H_{9}$). Throughout the thermal cracking reaction, C₂H₅· plays a crucial role. In addition, as observed in Fig. 1(A-D), the CH_4 conversion in the plasma + $Pt/ZrO_2 + T$ system is lower than in the plasma + Pt/ZrO_2 system because CH₄ is consistently produced in Stage 2. Ultimately, this results in 65.9 % selectivity for C_2H_4 and 60.5 % selectivity for H_2 with a residence time of 19.1 s in Stage 2.

4. Conclusion

We designed a hybrid plasma catalysis-thermal system, consisting of a coaxial DBD plasma stage followed by a thermal cracking stage, for the NOCM. By packing a Pt/ZrO₂ catalyst in the plasma, the system achieves an outstanding performance, i.e., 66 % C₂H₄ selectivity, 61 % H₂ selectivity and 28 % CH₄ conversion. The incorporation of 0.5 % Pt/ ZrO₂ catalyst within the DBD plasma reactor significantly enhances the CH₄ conversion (from 27 % to 29 %) and C–C coupling to C₂H₆ (from 43 % to 62 %), compared to the plasma alone system. The fresh and spent Pt/ZrO₂ catalyst was studied by XRD, HRTEM-STEM-EDX mapping, XPS, H₂-TPR, OES, and *in-situ* FTIR. The results indicate that the uniform high dispersion of metallic Pt⁰ promotes the dissociation of CH₄ into $\rm CH_{3^{\circ}}$ and subsequently facilitates C–C coupling to form $\rm C_2H_6$ in Stage 1. In stage 2, the product $\rm C_2H_6$ from Stage 1 serves as the reactant and is further converted to the targeted product $\rm C_2H_4$ through thermal cracking, ultimately leading to one of the highest yields of $\rm C_2H_4$ reported in literature, for either thermal or plasma catalysis, i.e., 18 %. In addition, the energy cost is 20397 kJ/mol. This hybrid plasma catalysis thermal system represents a promising and innovative method that combines non-thermal plasma with catalyst and thermal cracking, effectively overcoming the limitations associated with standalone plasma and thermal catalysis reactions.

CRediT authorship contribution statement

Rui Liu: Writing – review & editing, Writing – original draft, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. Eduardo Morais: Investigation, Methodology. Dongxing Li: Formal analysis, Data curation. Pengfei Liu: . Qian Chen: Methodology, Investigation. Shangkun Li: . Li Wang: Investigation. Xiaoxia Gao: Methodology, Investigation. Annemie Bogaerts: Writing – review & editing. Hongchen Guo: Validation, Supervision, Investigation. Yanhui Yi: Funding acquisition, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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