Optimization of Non-thermal Plasma-Assisted Catalytic Oxidation for Methane Emissions Abatement as an Exhaust Aftertreatment Technology

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Abstract
While methane-powered vehicles produce fewer greenhouse gas emissions in comparison to conventional fuel vehicles, there is a significant amount of methane slip in their exhaust that needs to be treated. This study investigates non-thermal plasma (NTP) assisted catalytic methane oxidation as an alternative method for the low temperature methane slip abatement applicable to the exhaust of biogas methane-powered vehicles. It is concluded that high CH4 conversion and CO2 selectivity can be obtained using NTP-catalysis at low temperature with Pd/Al2O3 found to be the most promising candidate among all catalysts tested. In addition, it was found that CH4 conversion efficiency was dependent on the feed gas components and gas hourly space velocity as well as how the activation energy is introduced. For example, a combination of plasma and external heat supply provides advantages in terms of CH4 conversion along with lower plasma energy consumption. The presence of N2 and O2 in the feed gas during NTP-catalytic methane oxidation results in unfavourable NOX formation which linearly increases with CH4 conversion. These results conclude that the most suitable aftertreatment option involves the combination of an oxidation catalyst with plasma to target the hydrocarbon and CH4 oxidation, followed by an ammonia-SCR system to convert the NOX formed in plasma assisted zone.

Keywords Methane oxidation · Pd/Al2O3 · Plasma DBD · NOx · NH3-SCR · Exhaust gas cleaning

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Introduction

Methane-powered vehicles have gained recent interest, with currently 23 million vehicles worldwide, due to their life cycle greenhouse gas (GHG) emissions benefits over conventional gasoline- and diesel-powered vehicles [1–3]. The use of methane as a fuel, either from fossil derived natural gas or renewable natural gas (biomethane), can reduce GHG emissions as well as other air pollutants. However, these benefits are mitigated by the presence of a significant amount of biogas derived-unburned methane (methane slip) in the engine exhaust [4], in particular during cold-start. Methane is a strong GHG with global warming potential which is 21 times higher than that of carbon dioxide. The low gas temperatures and the presence of impurities in the vehicle exhaust make the current catalytic converters inefficient for the methane removal and new and novel exhaust aftertreatment systems are required.

The thermal catalytic oxidation of methane has been extensively investigated [5–8]. However, even for the most active catalysts, 100% conversion cannot be achieved at temperatures below 400 °C, especially when water is present. An alternative approach to activate CH₄ at low temperatures is to utilize non-thermal plasma (NTP). Typically, gas phase NTP reactions are nonselective; however, combining an NTP with catalyst can improve the system performance in terms of conversion and product selectivity [9–11]. Most plasma-catalyst studies have used a dielectric barrier discharge (DBD) reactor [12–14] with one or more dielectric material and a catalyst that either filled the gap between the plasma electrodes or placed after the discharge zone. NTP-assisted catalytic systems, using different reactor configurations, have received a lot of attentions in the literature for various reactions including dry reforming of methane [15, 16], CO₂ hydrogenation [17, 18], NOₓ reduction [19] and the water–gas shift reaction [20]. Although there are a number of studies that have examined the NTP-assisted catalytic methane oxidation, few have studied it under conditions relevant to methane-powered vehicles exhaust applications [21, 22].

One of the concerns with plasma-catalyst systems for the methane oxidation is the benefits brought by the hybridization of the plasma and the catalyst. For example, the synergistic effect between the plasma and the catalyst for this reaction depends on several factors including the nature of power supply [21] and the reaction conditions [21–23]. While some researchers questioned such synergy and attributed the catalytic effect mostly to the subsequent CO oxidation [22], others reported a true synergistic effect on the CH₄ conversion [23]. An in-situ study of the role of the NTP in the hybrid catalytic reaction under CH₄ and CH₄+O₂ conditions has provided evidence that no significant structural changes occurred within the catalyst on application of the NTP and that the temperature of the Pd nanoparticles was lower than that necessary to activate the thermal CH₄ oxidation reaction [24]. Under similar conditions, using a diffuse reflectance infra-red Fourier transform spectroscopy coupled with mass spectrometer (DRIFTS-MS) cell, an enhancement in the formation of surface species on the Pd catalyst was reported [25]. Upon review of the body of work reported to date, the role of the catalyst during methane oxidation in the plasma-catalyst systems remains unclear. In addition, the effect of the components in a gas mixture that mimics the exhaust gas conditions, on the methane conversion and product selectivity needs to be clarified.

While the high endothermicity of the methane dissociation (434 kJ/mol) plays a crucial role in the plasma assisted reaction, the impact of high concentrations of H₂O, CO₂, O₂ and N₂/NOₓ has not been explored in detail. Baylet et al. [22] showed that an understanding of the undesirable side reactions in the plasma-only system, the role of CO₂ and water in the
plasma assisted catalytic process needs to be clarified. Moreover, the presence of N₂ and O₂ in the feed gas during plasma-assisted methane oxidation has been reported to result in NOX formation [22] and there are no reported investigation on the relationship between methane conversion and NOX formation in complex feed gas mixtures with the plasma-catalyst systems. In terms of temperature dependence, an increase in the reactor temperature to 200 °C was shown to have a positive effect on the CH₄ conversion [22]. Nozaki et al. [26] discussed that the dissociation of methane by electron impact was almost independent of the reaction temperature and that the vibrationally excited methane and water were the activated species at low temperature. Considering that the range of temperature experienced by the exhaust gas is wide, e.g. up to 300 °C when considering cold start conditions, the effect of temperature should be examined in more detail.

Previously, the NTP-assisted catalytic methane oxidation has only been explored using Pd/Al₂O₃, Al₂O₃, Ru/TiO₂ and Au/Al₂O₃ [27–29]. In order to investigate how the type of catalyst affects the performance of the plasma-catalyst and identify the best catalyst formulation for this reacting system, several supported metal catalysts were prepared and tested under the same reaction conditions. The selected catalysts in this study were among the ones reported for CH₄ activation for a wide range of reactions [30–33]. The aim of this study is to investigate the effect of the nature of the catalyst, the feed gas components as well as operating temperature conditions on the plasma-catalyst system performance in the methane oxidation reaction. Herein, an investigation of NOX production due to uncontrolled plasma reactions between N₂ and O₂ present in the gas stream and the link to methane conversion is established as well as strategies to mitigate NOX slip.

**Experimental and Methods**

**Catalyst Preparation**

The catalysts were prepared by incipient wetness impregnation. A NH₄-ZSM-5 (Zeolyst International, molar SiO₂/Al₂O₃ ratio of 30 and 80, approximately 0.17 cm³ g⁻¹ pore volume) was calcined in air at 550 °C for 8 h to obtain the H-ZSM-5 form (denoted ZSM-5). γ-Al₂O₃ was obtained from Sasol which had a pore volume of 0.5 cm³ g⁻¹ and this was dried in ambient air at 110 °C for 8 h. Both the ZSM-5 and γ-Al₂O₃ powders were pressed into pellets before being ground and sieved between 250 and 425 µm mesh sizes particles. The ZSM-5 or γ-Al₂O₃ supports were impregnated with solutions made by dissolving an appropriate amount of Co(NO₃)₂·6H₂O (99.999%, Sigma-Aldrich), Cu(NO₃)₂·xH₂O (99.999%, Sigma-Aldrich), Fe(NO₃)₃·9H₂O (≥ 98%, Sigma-Aldrich), LiNO₃ (99.99%, Sigma-Aldrich), (NH₄)₆Mo₇O₂₄·4H₂O (99.98%, Sigma-Aldrich), Ni(NO₃)₂·6H₂O (99.999%, Sigma-Aldrich) or Pd(NO₃)₂·2H₂O (99%, Sigma-Aldrich) in 10 wt% HNO₃ (prepared from concentrated HNO₃ (69–70%, BDH)) or diluting an appropriate amount of ruthenium (III) nitrosyl nitrate solution (1.5 wt% Ru, Ru(NO)(NO₃)₃(OH)ₓ x+y=3, Sigma-Aldrich) or rhodium (III) nitrate solution (10 wt% Rh, Rh(NO₃)₃, Sigma-Aldrich) in deionized water. After 48 h impregnation, the impregnated samples were dried in air at 110 °C for 8 h. The dried precursors were subsequently calcined in flowing air at 500 °C for 8 h following a temperature ramp of 10 °C min⁻¹ and then, cooled to room temperature before testing. The alumina-based catalysts were prepared to obtain 2 wt% nominal loading of Ru, Co, Fe, Cu, Rh, Pt, Ni or Li and 10 wt% nominal loading of Pd. A 2 wt% Pd/Al₂O₃ was also tested and was obtained from Johnson Matthey.
Experimental Setup

A schematic representation of the experimental setup is shown in Fig. 1. It consisted of a quartz tubular reactor (outside diameter (O.D.): 6 mm; inside diameter (I.D.): 4 mm) packed with different catalysts with a particle size in the range of 250–425 µm, operated in a plug flow mode. The NTP was generated in a DBD reactor configuration via a tungsten wire placed in the centre of the quartz tube as the ground electrode, insulated within a sealed quartz capillary tube (O.D.: 1.8 mm) to prevent arcing, and the power electrode (aluminium foil) wrapped on the outer surface of the reactor. The length of the discharge was determined by the length of the foil and was kept constant for all the experiments at 2 cm. This ensured that the plasma region entirely covered the packed bed, irrespective of the materials used.

An alternating current power supply (PVM500 model) was used to ignite the plasma. The electrical parameters were monitored using an oscilloscope (Tektronix MDO3022) connected to the reactor using a high voltage probe (Tektronix P6015A) to measure the applied voltage and a probe to measure the plasma current using a 10 Ω resistor. An example of a voltage-current profile associated to the plasma is shown in Fig. 2. An electric air blower heater (LE Mini Sensor Kit) with controllable temperature and air pressure was used to supply the external heat to the DBD reactor when plasma reactions at elevated temperatures were required. The reactor temperature as a function of the heater temperature at a constant air pressure was calibrated by replacing the ground electrode with a K-type thermocouple inside the DBD reactor in the absence of plasma.

The reactor feed containing the desired gas mixtures of CH₄, O₂, CO, CO₂, NO, NH₃ and Ar/N₂ (all gas cylinders were supplied by BOC, 99.99% purity) was supplied using mass flow controllers (Bronkhorst El flow). The H₂O vapor was added to the feed gas stream by passing Ar/N₂ as a carrier gas through a custom-made saturator at specific conditions.
temperature that was controlled using a Grant™ GD120 thermostatic bath. The produced water was removed from the gas stream after the reactor using a condenser, kept at 0 °C. All inlet and outlet gas lines were heat traced and maintained at 110 °C to prevent condensation. A gas chromatograph (GC; Agilent 7820A) was used to analyse the reactants and products and was equipped with a Porapak Q packed column and a flame ionization detector fitted with a methaniser to detect CO and CO$_2$. Propene, added post reactor and before the condenser to the effluent, was used as an internal standard. The concentration of NO$_x$ was measured with a Signal 4000 VM series analyser equipped with a chemiluminescence detector. When NH$_3$ was added to the feed gas, a Bruker Vertex 70 FTIR spectrometer fitted with a gas cell with a volume of 190 cm$^3$ was used for the analysis of reactants and products. An additional catalyst bed for NH$_3$-SCR, consisting of Cu-CHA provided by Johnson Matthey Technology was used in these experiments.

**Parameter Calculations**

The average power consumed during the plasma process was calculated by Eq. (1). The instantaneous current was estimated by measuring the voltage across the resistor (V$_r$), placed on the ground region (see Fig. 1) and having the resistance (R), i.e. 10 Ω, according to Eq. (2).

\[
P_{ave} = \frac{1}{T} \int_0^T V(t)I(t) \, dt
\]

\[
I(t) = \frac{V_r(t)}{R}
\]

where I was the current, $P_{ave}$ was the average power, t was time, T was a period, and V was the applied peak voltage. The specific input energy (SIE), representing the discharge energy density was calculated as the ratio of the average plasma power and the volumetric total gas flowrate at inlet.
In order to facilitate a comparison between plasma and thermal effects on the process an equivalent SIE for thermal systems was defined as the ratio of the thermal process heat duty \( Q \) in J s\(^{-1} \) and the volumetric total flowrate at inlet \([20, 21]\).

\[
SIE = \frac{Q}{\text{Volumetric total flowrate at inlet}}
\]

The heat duty for the thermal systems was assumed to be the sensible heat needed to bring the temperature of the gaseous reactants to the final reaction temperature. This assumption was based on the fact that the discharge plasma power was measured according to the amount of energy injected to the plasma system without considering the energy of reactions \([21]\). The heat duty was calculated using the Eq. (5).

\[
Q = \sum_{i=1}^{n} \int_{T_r}^{T_f} C_p \,dT
\]

where \( T_r \) was the room temperature (RT), \( T_f \) was the final reaction temperature and \( C_p \) was the heat capacity. The heat capacities for the gas components were calculated using equations from the literature (e.g. \([34]\)) for an ideal gas state as a function of temperature.

The \( \text{CH}_4 \) conversion and product selectivity were calculated using Eqs. 6 and 7, respectively:

\[
\text{CH}_4 \text{ conversion} = \frac{\text{CH}_4 \text{ molar flow rate at inlet} - \text{CH}_4 \text{ molar flow rate at outlet}}{\text{CH}_4 \text{ molar flow rate at inlet}}
\]

\[
\text{Product selectivity} = \frac{\text{Product molar flow rate at outlet}}{\text{CH}_4 \text{ molar flow rate at inlet} - \text{CH}_4 \text{ molar flow rate at outlet}}
\]

Given the atmospheric conditions in this study, the reactant and product gases were assumed to follow ideal gas law. The carbon balance \((\text{CH}_4 + \text{CO} + \text{CO}_2)\) was calculated and found to be close to 100% for all experiments. Only CO and \( \text{CO}_2 \) were observed as the carbon-based products for all the conditions investigated, therefore, the sum of CO and \( \text{CO}_2 \) selectivities were considered to be 100% to exclude small deviations. On the same basis, the \( \text{CO}_2 \) selectivity for experiments with \( \text{CO}_2 \) present in the feed was calculated using \( [\text{CO}_2 \text{ selectivity}] = 100 - [\text{CO selectivity}] \).

The errors associated with \( \text{CH}_4 \) conversion, CO/\( \text{CO}_2 \) selectivity and NO\(_X\) formation in this study were ±5%, ±4% and ±91 ppmv, respectively. The thermodynamic calculations to assess the stable reaction products at various conditions were performed in Aspen Plus V9 using the built-in Gibbs reactor package.

**Results and Discussion**

**Catalyst Screening**

The \( \text{CH}_4 \) conversion, CO/\( \text{CO}_2 \) selectivity and SIE results for the different catalysts prepared are reported in Table 1. Note that, while the catalysts reported in Table 1 are screened...
using one set of reaction conditions, the effect of varying the reaction conditions of the plasma-catalyst system is also further investigated for the best performing catalysts (see Sects. 3.2 and 3.3).

With zeolite-based materials, an increase in the molar SiO₂/Al₂O₃ ratio from 30 to 80 led to an increase in both CH₄ conversion and CO₂ selectivity from 48 to 65% and from 40 to 50%, respectively. The addition of Mo to both ZSM-5 (SiO₂/Al₂O₃ = 30 mol/mol) and ZSM-5 (SiO₂/Al₂O₃ = 80 mol/mol) enhanced the CH₄ conversion by 33% and 12% (up to 77% and 81%), respectively. The CO₂ selectivity stayed constant for the Mo/ZSM-5 (SiO₂/Al₂O₃ = 80 mol/mol) while for Mo/ZSM-5 (SiO₂/Al₂O₃ = 30 mol/mol), the CO₂ selectivity increased from 43 to 57%. The observed enhancement in conversion when Mo was added to the catalyst formulation could be related to the previously reported reactivity of molybdenum towards CH₄ activation [32, 35–40]. Mo/ZSM-5 has been applied to the methane aromatization reaction. This catalyst is bi-functional—methane is activated on the transition metal sites (Mo) to form intermediates which are further converted to aromatic compounds e.g. benzene on zeolite acidic sites [32]. As Mo is also active in partial oxidation reactions, e.g. oxidation of methanol to formaldehyde [36, 37], it is likely that in the presence of plasma, the methane could be partially oxidized and this could initiate a water gas shift-NTP reaction.

Over Al₂O₃, the NTP resulted in 79% CH₄ conversion and 86% CO₂ selectivity, a better performance when compared to the zeolite-based catalysts. Impregnating Pd on the Al₂O₃ support enhanced both the CH₄ conversion (up to 94–99%) and CO₂ selectivity (> 99%) with increasing precious metal loading (from 2 to 10 wt%). All other metals explored led to lower methane conversions than the pure alumina. The addition of Ru, Co, Cu, Rh and Pt led to a CO₂ selectivity similar or better than alumina; however, impregnation with Li, Fe or Ni resulted in significantly lower performance. It is likely that several reactions e.g. steam CH₄ reforming, partial oxidation, dry CH₄ reforming,

### Table 1

| Catalyst             | SIE, J mL⁻¹ | CH₄ conversion, % | Selectivity, % | CO₂ selectivity |
|----------------------|-------------|-------------------|----------------|-----------------|
| ZSM-5 (SiO₂/Al₂O₃ = 30) | 5.4         | 48                | 60             | 40              |
| ZSM-5 (SiO₂/Al₂O₃ = 80) | 5.3         | 65                | 50             | 50              |
| 2 wt% Mo/ZSM-5 (SiO₂/Al₂O₃ = 30) | 6.7         | 81                | 43             | 57              |
| 2 wt% Mo/ZSM-5 (SiO₂/Al₂O₃ = 80) | 6.2         | 77                | 57             | 43              |
| Al₂O₃                | 6.9         | 79                | 14             | 86              |
| 2 wt% Co/Al₂O₃       | 5.0         | 56                | 15             | 85              |
| 2 wt% Cu/Al₂O₃       | 4.9         | 48                | 8              | 92              |
| 2 wt% Fe/Al₂O₃       | 5.0         | 45                | 48             | 52              |
| 2 wt% Li/Al₂O₃       | 4.6         | 44                | 64             | 36              |
| 2 wt% Ni/Al₂O₃       | 4.7         | 45                | 41             | 59              |
| 2 wt% Pd/Al₂O₃       | 5.9         | 95                | 1              | 99              |
| 10 wt% Pd/Al₂O₃      | 5.1         | 99                | 1              | 99              |
| 2 wt% Pt/Al₂O₃       | 5.3         | 61                | 5              | 95              |
| 2 wt% Rh/Al₂O₃       | 5.4         | 46                | 8              | 92              |
| 2 wt% Ru/Al₂O₃       | 4.3         | 36                | 13             | 87              |
CO₂ methanation and H₂O-gas shift reaction occur simultaneously (with different rates) under the plasma-catalyst condition of this study, besides the CH₄ oxidation reaction (equations (S24) to (S35)). The active metals might promote side reactions resulting in an overall decrease in CO₂ selectivity and CH₄ conversion. For example, Gao et al. [41] have recently reported on the high-performance plasma enabled CO₂ methanation over bimetallic Ni–Fe catalysts using a nanosecond pulsed power supply. The low methane conversion and CO₂ selectivity observed with Fe, Li and Ni could indeed indicate that despite the known activity of these catalysts towards CO oxidation, in the presence of plasma, a number of side reactions take place.

As reported in Table 1, Pd/Al₂O₃ catalysts had the highest activity and selectivity in comparison to other catalysts tested. The Brunauer–Emmett–Teller (BET) surface area and X-ray diffraction (XRD) patterns for the Pd catalysts are reported in the ESI. It is noteworthy that Pd-based catalysts are known to have the best performance in thermal catalytic CH₄ oxidation [7, 42, 43]. Lee et al. [23] examined a 2 wt% Pd/Al₂O₃ powder catalyst in a fixed-bed reactor design during NTP-catalytic CH₄ oxidation at ambient temperature and obtained a significant increase in CH₄ conversion and CO₂ selectivity when adding the catalyst in the plasma zone, in line with the results of this study. Baylet et al. [22] compared the performance of post-plasma and in-plasma catalyst systems with plasma-only system for CH₄ combustion over a Pd/Al₂O₃/cordierite catalyst and reported that while CH₄ conversion remained the same for post-plasma catalyst and plasma-only systems, there was a significant decrease in CH₄ conversion for in-plasma catalyst system, attributed mainly to the lower residence time of the gas components when the catalyst was loaded in the discharge area. De Rosa et al. [21] reported a plasma-only, NTP-catalytic and thermal catalytic methane oxidation over a 2 wt% Pd/Al₂O₃ in 0.5 kPa CH₄, 10 kPa O₂, 5.5 kPa CO₂, 7 kPa H₂O in N₂ using a different reactor configuration, i.e. an alumina tube reactor with a stainless steel wire as the internal electrode, in comparison to the reactor configuration of this study. No synergistic effect on CH₄ conversion was observed when combining plasma and catalyst with an AC power supply although there was a synergistic effect on CH₄ conversion using a nanopulse power supply [21] and similar findings were reported by Nozaki et al. [26].

**In-situ** DRIFTS-MS studies revealed that the formation of surface species, e.g. carbonate and formate, was significantly affected by the plasma in the methane oxidation over a Pd catalyst in comparison to the thermal catalytic reactions [25]. In addition, temperature increases in the NTP-catalyst system have been observed and it was suggested that this process was not isothermal especially at high plasma SIEs [21, 24, 44]. De Rosa et al. [21] reported a linear relationship between the reactor temperature (up to 300 °C) and the SIE in the plasma-only and plasma catalyst systems. Molteni et al. [44] reported that the temperature rise induced by the plasma was significant during CH₄ oxidation reaction and this might lead to increased methane conversion. However, Gibson et al. [24] reported that the temperature rise in the bed was insufficient to lead to the thermal catalytic CH₄ conversion. Using an IR camera and EXAFS, it was found that during the CH₄ oxidation over a Pd/Al₂O₃ catalyst packed in the NTP zone, the temperature of the Pd nanoparticles was around 162 °C, i.e. below the temperature required for the activation of CH₄ (> 200 °C) [24]. The heat generated during plasma-induced CH₄ oxidation reaction, on the other hand, might promote the further oxidation of CO to form CO₂ over the catalyst, because temperatures below 200 °C are sufficient for CO oxidation over Pd/Al₂O₃ catalysts [45, 46].

The calculated SIE results, shown in Table 1, varied in the range of 4.3–6.9 J mL⁻¹ for different catalyst system even though the experiments in Table 1 were conducted under apparently identical reaction conditions (e.g. constant applied voltage and frequency). The
metals impregnated on the catalyst surface might be the source of variations in SIEs by changing the dielectric constant in the discharge zone [47].

**Effect of Gas Components and GHSV**

The effect of the reactant feed gas composition and GHSVs on the CH$_4$ conversion and CO/CO$_2$ selectivity over Al$_2$O$_3$ and 10 wt% Pd/Al$_2$O$_3$ catalyst is reported in Fig. 3. To further differentiate the effect of Pd metal on Al$_2$O$_3$ support, a catalyst with a higher loading of Pd (10 wt% Pd/Al$_2$O$_3$) was selected for the rest of study. The gas compositions consisted of:

- Condition (a): 0.5 kPa CH$_4$, 10 kPa O$_2$ in Ar;
- Condition (b): 0.5 kPa CH$_4$, 10 kPa O$_2$ in N$_2$;
- Condition (c): 0.5 kPa CH$_4$, 10 kPa O$_2$, 7 kPa H$_2$O, 5.5 kPa CO$_2$ and 0.1 kPa NO, in N$_2$.

With Ar as the balance gas, the conversion of CH$_4$ over the 10 wt% Pd/Al$_2$O$_3$ is high, e.g. 98% at GHSV = 171,429 mL g$^{-1}$ h$^{-1}$, and significantly higher than over Al$_2$O$_3$ at the same GHSV, e.g. 59% at GHSV = 171,429 mL g$^{-1}$ h$^{-1}$. An increase in the GHSV in the plasma-catalyst system reduced the overall residence time of the gas components, and the energy density, resulting in, as expected, lower conversions. As observed in Fig. 3, doubling the GHSV from 171,429 to 342,858 mL g$^{-1}$ h$^{-1}$ decreased the CH$_4$ conversion slightly for the 10 wt% Pd/Al$_2$O$_3$ from 98 to 96% and, significantly for Al$_2$O$_3$ from 59 to 43%. The CO$_2$ selectivity remained around 100% over the 10 wt% Pd/Al$_2$O$_3$ and decreased from 89 to 78% for Al$_2$O$_3$. It is believed that besides the electron-impact dissociation of CH$_4$ and O$_2$ in the plasma, the excited Ar species can dissociate CH$_4$ and O$_2$ through a “Penning dissociation” phenomenon which correlates to an energy transfer from excited species to other molecules [15, 48, 49]. The relatively small decrease in

![Fig. 3](image-url) Effect of feed gas composition and GHSV on NTP-catalytic CH$_4$ oxidation over 10 wt% Pd/Al$_2$O$_3$ at 7 kV, 30 kHz. (a and d) Condition (a): 0.5 kPa CH$_4$, 10 kPa O$_2$ in Ar; (b and e) Condition (b): 0.5 kPa CH$_4$, 10 kPa O$_2$ in N$_2$; (c and f) Condition (c): 0.5 kPa CH$_4$, 10 kPa O$_2$, 7 kPa H$_2$O, 5.5 kPa CO$_2$ and 0.1 kPa NO in N$_2$.
conversion of methane when increasing the GHSV could be attributed to the kinetically enhanced collisions between the excited noble gas atoms and methane molecules. As shown in Fig. 3b, if the GHSV is further increased, the positive effect of the gas phase chemistry is superseded by the reaction kinetics over the catalyst, represented by a ten-fold reduction in CH$_4$ conversion at the highest space velocity.

The impact of using N$_2$ as the balance gas on the CH$_4$ conversion was assessed with condition (b). At a similar GHSV, there was a decrease in the CH$_4$ conversion for both 10 wt% Pd/Al$_2$O$_3$ and Al$_2$O$_3$ catalysts when using N$_2$ instead of Ar as balance. The effect of N$_2$ was more pronounced at high GHSVs, e.g. at 342,858 mL g$^{-1}$ h$^{-1}$, the CH$_4$ conversion decreased from 96% for condition (a) to almost 10% for condition (b) over the 10 wt% Pd/Al$_2$O$_3$ catalyst. As discussed above, the Penning effect can account, to a certain extent, for the higher CH$_4$ conversion in Ar. While CO$_2$ selectivity remained above 90% over the 10 wt% Pd/Al$_2$O$_3$ for both conditions (a) and (b), it decreased significantly over the Al$_2$O$_3$ catalyst when replacing Ar with N$_2$ at a constant GHSV. For example, the CO$_2$ selectivity reduced from 89% at condition (a) to 58% at condition (b) when GHSV was 171,429 mL g$^{-1}$ h$^{-1}$ and Al$_2$O$_3$ was used as the catalyst.

Modeling studies for a mixture of CO$_2$/CH$_4$/N$_2$ (1:1:8) have shown that the dissociation of CH$_4$ and CO$_2$ splitting to CO and O are promoted by the metastable singlet and triplet states generated by electron impact excitation of N$_2$, which enhances CH$_4$ and CO$_2$ conversions [50] (equations listed in ESI, Section S2). This effect is not observed for CH$_4$ conversion in this study but the decrease in CO$_2$ selectivity over Al$_2$O$_3$ by switching to N$_2$ balance could be attributed to the collision of some of the generated CO$_2$ molecules with metastable N$_2$.

When a complex gas mixture containing CH$_4$, O$_2$, CO$_2$, H$_2$O, NO and N$_2$ balance [condition (c)] was tested over the 10 wt% Pd/Al$_2$O$_3$ catalyst, the methane conversion remained high, with less than 10% decrease compared to the simpler gas mixtures used in conditions (a) and (b). For example, at a GHSV of 171,429 mL g$^{-1}$ h$^{-1}$ when changing the feed composition from condition (a) to (b) and (c), the methane conversion was 97.7, 96.1 and 89.7%, respectively, while the CO$_2$ selectivity remained very high (above 98%) in all cases. In contrast, when using Al$_2$O$_3$, the CH$_4$ conversion increased in condition (c) compared with condition (b), from 25 to 43% at GHSV of 171,429 mL g$^{-1}$ h$^{-1}$. In line with the Al$_2$O$_3$ results, an improvement in CH$_4$ conversion using condition (c) gas was also observed in comparison to condition (b). However, the CO$_2$ selectivity reduced significantly when switching to condition (c) over Al$_2$O$_3$, compared with condition (b), from 58% to −11% at GHSV of 171,429 mL g$^{-1}$ h$^{-1}$. Note that the negative CO$_2$ selectivity indicates that some of the inlet CO$_2$ was converted during the plasma reaction, for example through methane reforming, as discussed in [22]. This would be consistent with the observed increase in CO selectivity.

Under thermal conditions, it is known that the Pd catalyst activity is inhibited by the presence of combustion products e.g. H$_2$O or CO$_2$ [6, 42] which may also be the reason for the small decrease in conversion under NTP conditions observed with the 10 wt% Pd/Al$_2$O$_3$ catalyst. Similarly, the addition of H$_2$O to the plasma-assisted catalytic toluene oxidation was shown to have a negative effect on catalyst activity, and was attributed to the competitive adsorption of water and also to a change in the plasma discharge behavior through quenching energetic electrons and reactive species [51, 52]. However, a previous study observed a promotional effect of H$_2$O addition to the plasma-assisted catalytic CO oxidation through facilitating the decomposition of carbonate species on the Cu/Ce catalyst and enhancing catalyst stability [53].
When considering different feed compositions and reaction conditions, it can be concluded that, for the current study, a promotional effect of the addition of Pd compared to the support alone was also observed, both in terms of CH$_4$ conversion and CO$_2$ selectivity.

**Effect of External Heat Supply and Plasma Energy**

To evaluate the effect of combining an external heat source with the NTP to activate the catalyst for the CH$_4$ oxidation reaction, a heat blower was used to control the reactor temperature up to 300 °C. The performance of the NTP-catalytic CH$_4$ oxidation over the 10 wt% Pd/Al$_2$O$_3$ with a feed composition of 0.5 kPa CH$_4$, 10 kPa O$_2$, 7 kPa H$_2$O, 5.5 kPa CO$_2$ and 0.1 kPa NO in N$_2$ as a function of reactor temperature and plasma SIE is reported in Fig. 4. The variation in plasma SIE from 1.1 to around 4.9 J mL$^{-1}$ is the result of a change in the applied peak voltage from 5 to 7 kV at a constant frequency of 30 kHz. The plasma SIE followed a linear relationship with the applied voltage as shown in Fig. S2. As the applied voltage increased there was also an increase in the reactor temperature which contributed to a small increase in the plasma SIE, presented in Fig. S3. For example, at 7 kV and 30 kHz, the plasma SIE increased from around 3.7 to 4.7 J mL$^{-1}$ when the temperature increased from RT to 300 °C.

Because CH$_4$ is a more stable molecule compared to other hydrocarbons, due to the strength of the C–H bonds, it requires high temperatures or energies to be activated. Typically, the thermal catalytic CH$_4$ oxidation over supported Pd catalysts is initiated at temperatures above 200 °C and often only reaches 100% CH$_4$ conversion at 400 °C or above [24, 42]. Examining CH$_4$ oxidation reaction over the 10 w% Pd/Al$_2$O$_3$ at the operating conditions shown in Fig. 4, in the thermal mode (no plasma), no CH$_4$ conversion from RT to 250 °C took place and only 4% CH$_4$ conversion was observed at 300 °C. The limited CH$_4$ conversion at 300 °C in this study may be attributed to the presence of H$_2$O and CO$_2$ in the gas feed which act as poisons [6, 42]. From Fig. 4a it is observed that an increase in plasma SIE and temperature led to an enhancement of the CH$_4$ conversion. For example, at a constant plasma SIE of 1.5 J mL$^{-1}$, an increase in temperature from RT to 300 °C increased the CH$_4$ conversion from 0 to 98%. Similarly, without external heat supply (at RT in Fig. 4a), increasing the plasma SIE from 1.2 to 3.7 J mL$^{-1}$ improved the CH$_4$ conversion.

![Fig. 4](https://example.com/fig4.png)

**Fig. 4** CH$_4$ conversion (a) and CO$_2$ selectivity (b) as a function of temperature and plasma SIE in NTP-catalytic CH$_4$ oxidation (the lines are only to guide the eye). Reaction conditions: 10 wt% Pd/Al$_2$O$_3$, 0.5 kPa CH$_4$, 10 kPa O$_2$, 7 kPa H$_2$O, 5.5 kPa CO$_2$ and 0.1 kPa NO in N$_2$, 171,429 mL g$^{-1}$ h$^{-1}$ GHSV
conversion from almost 0 to 90%. The plasma-assisted catalytic process without external heat contribution can activate CH$_4$ at RT and very high conversion of CH$_4$ to products can be achieved with an increase in plasma SIE. Similar effect of the plasma SIE on CH$_4$ conversion during plasma-only CH$_4$ oxidation was reported [23].

Increasing the plasma SIE and temperature also enhanced the CO$_2$ selectivity over the 10 wt% Pd/Al$_2$O$_3$ catalyst as shown in Fig. 4b. The CO$_2$ selectivity was above 90% once the CH$_4$ conversion was greater than 10%. Once the Pd catalyst became activated in the reaction, through heat supply or plasma, the CO$_2$ selectivity reached around 100%. Conversely, at low temperatures (< 150 °C) and plasma SIEs (e.g. 1.1 J mL$^{-1}$) where the CH$_4$ conversion is below 10%, other reactions such as steam reforming of methane or dry reforming of methane govern the conversion, as also discussed in Sect. 3.2, and resulted in negative or low CO$_2$ selectivities. In agreement with these results, Pham Huu et al. [28] reported a shift in CH$_4$ conversion towards lower light-off temperatures when using plasma-assisted catalytic CH$_4$ oxidation with in-plasma and post-plasma configurations in comparison to thermal catalytic reaction and plasma alone.

To achieve the same level of CH$_4$ conversion in a plasma-catalyst system, the applied peak voltage and reactor temperature can be tuned, as shown in Table 2. From an energy perspective, increasing the external heat supply significantly reduced the plasma energy and total energy required to obtain the same CH$_4$ conversion. For example, the plasma SIE required to obtain 50% CH$_4$ conversion, reduced from 3.1 to 1.3 J mL$^{-1}$ resulting in the total SIE reducing from 3.1 to 1.6 J mL$^{-1}$ when the temperature increased from RT to 260 °C, respectively. Similarly, a decrease in plasma SIE from 3.7 to 1.6 J mL$^{-1}$ required an increase in the temperature from RT to 293 °C to obtain 90% CH$_4$ conversion at the reactor outlet, leading to a decrease in total SIE from 3.7 to 1.9 J mL$^{-1}$. In summary, a combination of plasma and external heat supply in a plasma-catalyst gives access to high CH$_4$ conversion with lower energy consumption.

The results in Table 2 also indicate that the external heat is more efficient than the plasma at initiating the methane oxidation reaction, in line with the results reported by [21]. However, it is worth noting that, in a practical application, the heat is dependent on the exhaust gas temperature, which leads to inefficient cold start emission control using traditional approaches. Under such conditions, where the heat supply is low, plasma could be used as it is almost instantaneous in its onset. As shown in Fig. S4, a process control with time dependent regulation (decrease) of the plasma SIE could guarantee methane emission abatement while minimizing the energy penalty by tuning the SIE from the NTP.

**Table 2** Obtaining the same level CH$_4$ conversion as a function of temperature and applied voltage. Data were extracted from Fig. 4

| Applied voltage, kV | Temperature, °C | 50% CH$_4$ conversion SIE, J mL$^{-1}$ | Applied voltage, kV | Temperature, °C | 90% CH$_4$ conversion SIE, J mL$^{-1}$ |
|---------------------|-----------------|----------------------------------------|---------------------|-----------------|----------------------------------------|
|                     |                 | Thermal | Plasma | Total       |                     | Thermal | Plasma | Total       |
| 6.5                 | RT              | 0       | 3.1    | 3.1         | 7.0                 | RT       | 0       | 3.7         | 3.7         |
| 6.0                 | 161             | 0.17    | 2.6    | 2.8         | 6.5                 | 164      | 0.17    | 3.2         | 3.4         |
| 5.5                 | 217             | 0.24    | 1.8    | 2.0         | 6.0                 | 221      | 0.24    | 2.9         | 3.1         |
| 5.0                 | 260             | 0.29    | 1.3    | 1.6         | 5.5                 | 244      | 0.27    | 2.0         | 2.3         |
| –                   | –               | –       | –      | –           | 5.0                 | 293      | 0.33    | 1.6         | 1.9         |
Together with the CH₄ conversion and CO₂ selectivity, the effect of plasma on NOₓ formation/conversion needs to be considered in after-treatment applications. The presence of N₂ as the balance gas resulted in the production of a combination of NO and NO₂ in the plasma discharge zone (Table 3). The amount of NOₓ produced was 836 ppmv in the presence of the Pd/Al₂O₃ catalyst while the use of Al₂O₃ support in the plasma zone resulted in a decrease in NOₓ formation to 644 ppmv. These changes also reflected changes in the CH₄ conversion with high NOₓ formation occurring at high CH₄ conversions, as a result of the increase in electric field intensity. This consequently lead to an increase in the rate of formation of active species (such as N, O, CH₃) through electron impact reactions, and the effective collisions between them (equations listed in ESI, section S2). Moreover, the NO/NO₂ ratio also varied and increased in the following order: Al₂O₃ < Pd/Al₂O₃. Under the conditions of this study, thermodynamic calculations suggest that only NO is a stable product of N₂ and O₂ reaction, especially at high SIEs. This indicates that the plasma provides non-equilibrium conditions with generation of a mixture of NO and NO₂.

The effect of the reaction conditions on the CH₄ conversion and NOₓ formation over the 10 wt% Pd/Al₂O₃ is reported in Table 4. Under condition (c), the feed gas contained 1000 ppmv NOₓ (corresponding to 0.1 kPa NO) and the effluent data indicated the formation of an additional 224 ppmv NOₓ during the plasma-catalytic reaction. This reflected a decrease in the amount of NOₓ formed in the plasma in comparison to condition (b) due to the addition of NO in the feed gas. These preliminary results seemed to indicate that the presence of NO in the feed gas led to reduced formation of NOₓ. However, when the reactor temperature was increased to 300 °C (condition (d)), the formation of NOₓ in the DBD increased to 714 ppmv, to a total of 1714 ppmv outlet concentration. This is consistent with the reported formation of NOₓ (mainly from plasma gas phase reactions via Eqs. (8, 9, 10, 11, 12, and 13)).

Table 3  CH₄ conversion and NOₓ formation in plasma discharge; 7 kV, 30 kHz, 0.5 kPa CH₄, 10 kPa O₂ in N₂, GHSV = 171,429 mL g⁻¹ h⁻¹

| Catalyst   | CH₄ conversion % | NO ppmv | NO₂ ppmv | NOₓ ppmv | NO/NO₂ |
|------------|-----------------|---------|----------|----------|--------|
| Al₂O₃      | 25              | 388     | 257      | 644      | 1.51   |
| 10% Pd/Al₂O₃ | 96              | 524     | 311      | 836      | 1.68   |

Table 4  CH₄ conversion and NOₓ formation in plasma discharge as function of reaction conditions over 10 wt% Pd/Al₂O₃ at 7 kV, 30 kHz. All conditions were tested at GHSV of 171,429 mL g⁻¹ h⁻¹

| Condition | Temperature, °C | Feed gas composition | CH₄ conversion, % | Outlet NOₓ concentration, ppmv |
|-----------|-----------------|----------------------|-------------------|--------------------------------|
| b         | RT              | 0.5 kPa CH₄ and 10 kPa O₂ in N₂ | 96 | 836 |
| c         | RT              | 0.5 kPa CH₄, 10 kPa O₂, 5.5 kPa CO₂, 7 kPa H₂O and 0.1 kPa NO in N₂ | 90 | 1224 |
| d         | 300             | 0.5 kPa CH₄, 10 kPa O₂, 5.5 kPa CO₂, 7 kPa H₂O and 0.1 kPa NO in N₂ | 100 | 1714 |

NOX Production and Mitigation Strategies
being enhanced even if NO is already present in the feed. These results are in good agreement with those reported in [54], which attributed this behaviour to the fact that a 10% oxygen concentration in the feed is above the critical oxygen concentration range, leading to an increase in the NO\textsubscript{X} concentration with the energy density. The present results also indicate that the energy density dependence is driven by both the plasma and heat. The general trend reported in Fig. 5 appears to indicate a good correlation between the CH\textsubscript{4} conversion and the effluent NO\textsubscript{X} concentration, for all the catalysts tested in this study, irrespective of reaction conditions. The results, herein, also indicate that the simultaneous NO\textsubscript{X} reduction and methane oxidation is not possible within the conditions investigated due to the electron impact dissociation of N\textsubscript{2} and O\textsubscript{2} (Eqs. (8, 9, and 10)) and the subsequent reactions that occur between the active species, some of which are listed in ESI Section S2 [22, 50–56].

\begin{align}
e^{-} + \text{N}_2 &\rightarrow e^{-} + \text{N} + \text{N} \\
e^{-} + \text{O}_2 &\rightarrow e^{-} + \text{O} + \text{O} \\
e^{-} + \text{NO} &\rightarrow e^{-} + \text{O} + \text{N} \\
\text{O} + \text{O}_2 &\rightarrow \text{O}_3 \\
\text{N} + \text{O}_2 &\rightarrow \text{NO} + \text{O}
\end{align}

**Fig. 5** CH\textsubscript{4} conversion as a function of NO\textsubscript{X} formation over all catalysts tested in this study at different reaction conditions. Note NO is not added to the gas feed in any of the tests in this figure. (Green Inverted triangle) ZSM-5 (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 30); (Blue triangle) ZSM-5 (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 80); (Golden brown Left pointer triangle) 2 wt% Mo/ZSM-5 (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 30); (Diamond) 2 wt% Mo/ZSM-5 (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 80); (Red circle) Al\textsubscript{2}O\textsubscript{3}; (Brown Hexagon) 2 wt% Co/Al\textsubscript{2}O\textsubscript{3}; (Orange pentagon) 2 wt% Cu/Al\textsubscript{2}O\textsubscript{3}; (Star) 2 wt% Fe/Al\textsubscript{2}O\textsubscript{3}; (Orange asterisk) 2 wt% Li/Al\textsubscript{2}O\textsubscript{3}; (Multiplication symbol) 2 wt% Ni/Al\textsubscript{2}O\textsubscript{3}; (Black square box) 2 wt% Pd/Al\textsubscript{2}O\textsubscript{3}; (Minus symbol) 10 wt% Pd/Al\textsubscript{2}O\textsubscript{3}; (Plus symbol) 2 wt% Pt/Al\textsubscript{2}O\textsubscript{3}; (Vertical blue line) 2 wt% Rh/Al\textsubscript{2}O\textsubscript{3}; (Cyan right pointer triangle) 2 wt% Ru/Al\textsubscript{2}O\textsubscript{3} (Color figure online)
To address this challenge and to mitigate for the NO\textsubscript{X} formation, a different approach was explored, whereby the addition of ammonia and a suitable SCR catalyst was considered. While NH\textsubscript{3}-SCR (Eqs. (14, 15, and 16)) is a mature technology, it is not suitable for simultaneous conversion of methane and NO\textsubscript{X} under realistic conditions during cold start [57].

\begin{align*}
O + N &\rightarrow NO \quad (13) \\
4\text{NH}_3 + 6\text{NO} &\rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \text{ slow SCR} \quad (14) \\
4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 &\rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \text{ fast SCR} \quad (15) \\
4\text{NH}_3 + 4\text{NO} + \text{O}_2 &\rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \text{ standard SCR} \quad (16)
\end{align*}

The catalyst of choice for the SCR process is a commercially available system, Cu-CHA from Johnson Matthey Technology. A typical thermal activation light-off experiment is reported in Fig. 6. As expected and reported in the literature [58], the activity of the Cu-CHA catalyst for NO\textsubscript{X} reduction was found to be high, with 100% conversion achieved at 190 °C under standard thermal activation. As noted earlier, the conversion of methane under these conditions is negligible below 400 °C, as illustrated in Fig. 6. Thus, an assessment of the effect of plasma on the simultaneous reduction of NO\textsubscript{X} and CH\textsubscript{4} oxidation during cold start using NH\textsubscript{3} as a reducing agent was examined.

For a better understanding of the formation and evolution of the reaction products/intermediates during the plasma exposure, without the interference from high concentrations of H\textsubscript{2}O and CO\textsubscript{2}, the inlet feed was simplified (CH\textsubscript{4}, O\textsubscript{2}, NO and NH\textsubscript{3} with N\textsubscript{2} balance) and the outlet line of the reactor was connected directly to an FTIR. The following vibrational bands were used as diagnostics for the presence of different species: CH\textsubscript{4} at 3016 and 1304 cm\textsuperscript{-1}, CO\textsubscript{2} at 2360 cm\textsuperscript{-1}, CO at 2143 cm\textsuperscript{-1}, NO at 1883 cm\textsuperscript{-1}, NO\textsubscript{2} at 1614 cm\textsuperscript{-1}, N\textsubscript{2}O at 2223 cm\textsuperscript{-1}, HNO\textsubscript{3} at 1325 and 1718 cm\textsuperscript{-1} [56].

![Fig. 6 NO (red) and CH\textsubscript{4} conversions (blue) as function of reactor temperature using a commercial Cu-CHA catalyst. Reaction conditions: 0.5 kPa CH\textsubscript{4}, 10 kPa O\textsubscript{2}, 0.1 kPa NO, and 0.1 kPa NH\textsubscript{3} in Ar, GHSV = 85,714 mL g\textsuperscript{-1} h\textsuperscript{-1} (Color figure online)]
Figure 7 reports the FTIR spectra of the reactants and products from the DBD reactor with the addition of Cu-CHA to the discharge, at 2.1–2.3 J mL⁻¹. When the plasma is ignited, a 40% reduction in the methane concentration was observed and a decrease in the intensity of NO band. However, since the NO₂ concentration simultaneously increased, very little change was observed in the overall NOₓ conversion indicating that the NO was oxidised to NO₂. This is in good agreement with [54]. Nitrous oxide was also formed in the plasma discharge (equations (S6) to (S9)), with concentration of approximately 430 ppmv N₂O. Wang and Tokunaga [54, 59] reported that in the presence of a high concentration of O radicals and O₂, both NOₓ and N₂O are formed in plasma (equations (S1) to (S25)). It should, however, be noted that the increase of the peaks at 2210–2250 cm⁻¹ might not be entirely due to N₂O formation, but also to other -NCO species.

To prevent the NH₃ from being oxidised in the plasma instead of being utilised as a reducing agent, a hybrid solution was further explored. It made use of a hybrid dual-stage reactor where the oxidation reactions took place upstream in the plasma discharge (in-plasma catalysis (IPC)) and the SCR catalyst and NH₃ injection were located downstream, i.e. in a post-plasma catalysis (PPC) configuration, as shown in Fig. 8 (with further details in Fig. S5). This configuration benefited from the supply of a small amount of heat from the methane oxidation zone to the SCR region.
The dual stage configuration resulted in a full methane conversion with >99% CO₂ selectivity, as evidenced in Fig. 9 from the disappearance of the bands at 3016 and 1304 cm⁻¹, and the increase of the CO₂ feature at 2360 cm⁻¹, respectively. Once NH₃ was injected downstream of the plasma reactor, the NOₓ were fully converted, as shown by the disappearance of the NO and NO₂ bands. No significant change was observed in the intensity of the band at 2223 cm⁻¹ when compared to the one in Fig. 7 (417 ppmv N₂O), which indicated that this species is produced in the plasma discharge and the catalysts used herein did not promote the formation nor the removal of this product. Zhao et al. [60] have shown a strong correlation between the SIE and N₂O formation when a V₂O₅-WO₃/TiO₂ catalyst was used. In our previous study on HC-SCR [19] we have shown that the N₂O selectivity is dependent on the applied frequency, temperature and NOx conversion and we have proposed that the duration of the pulse can be of high importance, as also discussed by de Rosa et al. [21] While N₂O slip is highly undesirable, the current study was not intended for exhaustive mitigation strategies but rather to put forward a possible solution for cold-start CH₄ and NOX emission control for diesel engines.

As demonstrated in the present study, the main disadvantage of using an in-plasma catalyst discharge to reach complete oxidation of the methane under realistic exhaust conditions was the formation or low conversion of NOX (Eqs. (8, 9, 10, 11, 12, and 13) and (S1) to (S25)).

It was found that the concentration of oxygen in the feed had a critical role on the NTP denitration performance [54] and, while high conversions of NOX can be achieved with O₂ concentration lower than 1%, this is not realistic for automotive exhaust conditions. It is important to note that the addition of water and ammonia is beneficial towards the NOX removal efficiency even with O₂ concentrations > 10% as long as the SIE is kept below 2 J mL⁻¹, as shown by Wang et al. It is suggested that, as soon as the SIE increases, allowing for more reactive oxygen species (ROS) to be formed, the removal efficiency becomes negative, with reactions (Eqs. (12), (13)) more prone to take place. Furthermore, the interaction between the excited NO* and other N-containing species formed in the plasma and on the oxide ions at the catalyst surface, gives rise to –NOₓ and –NO₂ species, which could lead to an increase in the overall NOₓ concentration, resulting therefore in a negative NOₓ removal efficiency [54, 61]. The ease of –N radicals formation is of paramount importance in terms of NOₓ concentration and it might be that a different way of generating plasma
instead of the DBD method could indeed lead to significant differences in NOX concentration, as seen in [54].

The properties observed for the combined hybrid system indicate that the use of the NTP + catalyst closely followed by an ammonia-SCR system may hold the solution to diesel cold start emission control, as proposed in Fig. 10.

Conclusions

This paper reports on the NTP-catalytic methane oxidation as an aftertreatment technology to remove methane emissions in the exhaust of methane-powered vehicles. High CH4 conversion and CO2 selectivities can be achieved with the presence of a catalyst in a DBD reactor. The CO2 selectivity during NTP-catalytic CH4 oxidation is related to the CH4 conversion and increases linearly with the CH4 conversion. In agreement with thermal catalysis, Pd/Al2O3 catalysts are shown to have the best performance for the NTP-catalytic methane oxidation in terms of CH4 conversion and CO2 selectivity among all catalysts tested. The performance of the plasma-catalyst system is found to depend on feed gas components and GHSVs. Complex gas mixtures that simulate real exhaust conditions can reduce methane conversion when using Pd/Al2O3 catalysts. A combination of plasma and external heat supply in a plasma-catalyst system can achieve high CH4 conversion and CO2 selectivity with lower energy consumption. This is an approach that appears particularly suitable to cold-start conditions using biogas as a fuel. The presence of N2 and O2 in the plasma system can lead to unfavorable NOX formation, which is not preventable as long as the plasma exists due to electron-impact dissociation reaction of these molecules. The NOX formation has a linear dependence with CH4 conversion during NTP-catalytic CH4 oxidation. The addition of a second catalyst bed, post-plasma, where NH3 can be injected for selectively reduce the nitrogen oxides at temperatures below 200 °C was shown to be an efficient solution in this case.

It is concluded that the most suitable aftertreatment option involves the combination of an oxidation catalyst with plasma to target the hydrocarbon and CH4 oxidation, followed by the NH3-SCR system to convert the NOX.

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**Declarations**

**Conflict of interest** The authors report no declaration of interest.

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