Characterization of plasma catalytic decomposition of methane: role of atomic O and reaction mechanism

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Abstract

In this work, we investigated atmospheric pressure plasma jet (APPJ)-assisted methane oxidation over a Ni-SiO_2/Al_2O_3 catalyst. We evaluated possible reaction mechanisms by analyzing the correlation of gas phase, surface and plasma-produced species. Plasma feed gas compositions, plasma powers, and catalyst temperatures were varied to expand the experimental parameters. Real-time Fourier-transform infrared spectroscopy (FTIR) was applied to quantify gas phase species from the reactions. The reactive incident fluxes generated by plasma were measured by molecular beam mass spectroscopy (MBMS) using an identical APPJ operating at the same conditions. A strong correlation of the quantified fluxes of plasma-produced atomic oxygen with that of CH_4 consumption, and CO and CO_2 formation implies that O atoms play an essential role in CH_4 oxidation for the investigated conditions. With the integration of APPJ, the apparent activation energy was lowered and a synergistic effect of 30% was observed. We also performed in-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) to analyze the catalyst surface. The surface analysis showed that surface CO abundance mirrored the surface coverage of CH_n at 25 ºC. This suggests that CH_n adsorbed on the catalyst surface as an intermediate species that was subsequently transformed into surface CO. We observed very little surface CH_n absorbance at 500 ºC, while a ten-fold increase of surface CO and stronger CO_2 absorption were seen. This indicates that for a nickel catalyst at 500 ºC, the dissociation of CH_4 to CH_n may be the rate-determining step in the plasma-assisted CH_4 oxidation for our conditions. We also found the CO vibrational frequency changes from 2143 cm^{-1} for gas phase CO to 2196 cm^{-1} for CO on a 25 ºC catalyst surface, whereas the frequency of CO on a 500 ºC catalyst was

2188 cm^{-1}. The change in CO vibrational frequency may be related to the oxidation of the catalyst.

1. Introduction

Plasma catalysis is a promising technique that may improve the efficiency of chemical processing using catalyst materials [1-3], and lower the temperature required to activate the catalyst [4, 5]. Plasma catalysis has been investigated for volatile organic compound (VOC) removal [6, 7], hydrocarbon reforming [8-11], ammonia production [12, 13] and others. Plasmas have also been used to synthesize catalysts [14, 15]. A synergistic effect, i.e., a higher conversion rate and lower activation energy for a combined approach relative to separate plasma or thermal catalysis driven conversions, have been reported in several publications [9, 16]. However, the mechanistic origins of the plasma-catalyst synergistic effect remain elusive.

Cold atmospheric pressure plasmas (CAPP) used in plasma catalysis are able to generate high energy electrons [17], ions, and highly reactive species including radicals and electronically excited species without large increase in gas temperatures [18-20]. This large variety of reactive species including the production of photons and electrical fields has not allowed to experimentally identify key species produced from the plasma that are responsible for plasma catalytic reactions [19]. The absence of such a correlation impedes the further development of the plasma-catalysis technique.

The methane oxidation to syngas reaction has many potential benefits compared to other methane reforming techniques [21]. Primarily, it is an exothermic reaction with a lower energy cost than other pathways [22]. Despite intense research efforts, the reaction pathways even without the presence of plasma remain subject to continued research. Two reaction pathways are mainly discussed: (i) Reforming mechanism: the CH_4 is first completely oxidized to CO_2 over the catalyst. Subsequently, CO_2 reforming of CH_4 takes place to produce CO, which is the secondary product [22-24]. (ii) Direct partial oxidation mechanism: CH_4 is dehydrated to CH_n

species on the catalyst which are then oxidized to CO, and CO is the primary product [25-28]. It should be noted that the temperature range and the state of the catalyst, e.g., reduced or unreduced, can have a significant influence on reaction pathways. The lack of a complete understanding of the pathways of thermal oxidation of CH_4 sets an obstacle for interpreting the mechanism of plasma-assisted CH_4 oxidation.

One of the difficulties in investigating the mechanism of plasma catalysis is the implementation of in-situ/operando surface characterization [29]. The rapid changes that occur on the catalyst surface can provide valuable information regarding the reaction pathways. However, the appearance of those surface species may be subtle and transient, making it difficult to capture such information, especially in the plasma-catalysis system where the plasma is generated in close contact with the catalyst providing challenges to perform in-situ surface characterization techniques. The high pressure environment also precludes the use of many surface characterization techniques standardly used in low pressure plasmas which require a vacuum environment [29]. Stere et al. described a novel design of a DBD plasma-catalysis system that allows in-situ surface characterization by DRIFTS to investigate plasma-assisted VOCs removal over three metal oxide catalysts [30].

In the past few years, we have developed a well-described non-thermal atmospheric pressure plasma jet [17, 20, 31, 32]-catalyst system that is capable of performing real-time downstream gas phase and operando surface analysis [11, 16, 29]. The key feature of such a design is the possibility to do in-situ surface characterization by DRIFTS. Since the plasma generation occurs remotely in the plasma jet and reactive species are convectively transported to the catalyst, easy access to the catalyst surface for external characterization is available. This approach has also key advantages for the measurement of the plasma-produced short-lived reactive species. The

APPJ-catalyst interaction in the decomposition of methane in this system has been extensively evaluated. Knoll et al. [16] investigated the behaviors of CH_4 and products of the reaction using different plasma parameters and catalyst temperatures. They found that the CO production was due primarily to the APPJ effect. The CO production was suppressed at high temperature while CO_2 production was enhanced. Spectral features obtained by DRIFTS were discussed and CO and CO_2 gases were found to be related with surface species. Zhang et al. [11] investigated the time-resolved response of surface CO and CH_n species to catalyst temperature, plasma feed gas composition, and plasma-surface distance. They found that the surface CO formation was correlated with the removal of surface CH_n by the APPJ when operating with high oxygen concentration in the feed gas.

Although much progress and understanding of the plasma-catalyst interaction have been accomplished, a comprehensive analysis of the connection between the plasma source and the plasma-catalytic reaction is still lacking. In this work, we characterized the downstream gas phase and the surface under various conditions using an IR spectrometer at the University of Maryland and quantified the plasma-produced reactive species flux using MBMS on an identical plasma jet operating at the same conditions at the University of Minnesota. A correlation between the measured gas phase species, reactive species produced by the APPJ, and surface species has been established, and the synergy effect has been evaluated. By combining all the measurements and performing correlations, we can draw conclusions about the key species contributing to the oxidation of CH_4 and shed light on the mechanism of the underpinning plasma-catalyst interaction.

2. Experimental setup and procedure

The plasma source used in this study was a RF driven APPJ running at 14.3 MHz frequency modulated by 20 kHz on/off duty cycle (20% on time and 80% off time). A high voltage tungsten pin was placed in the center of a dielectric quartz tube, whereas the grounded ring electrode was attached around the tube [16]. The properties of this APPJ have been extensively reported [17, 33, 34]. The APPJ was fed with 200 sccm Ar and 1, 2 or 3 sccm O_2, corresponding to 0.5%, 1.0% and 1.5% O_2.

The catalyst used in the experiments was a nickel catalyst supported by alumina (13 wt%) and silica (12 wt%). The weight percentage of nickel was 65%. To compare with the nickel catalyst, kieselguhr, a powder material, whose amorphous silica composition is over 95 wt%, was used as a control to study the plasma effect without the presence of a metal catalyst. More detailed information regarding the catalyst material can be found in [11].

A schematic of the plasma system is shown in figure 1. The APPJ was integrated in a high temperature reaction chamber (HVC-DRM-5) by a lab-made macro feedthrough, which was fixed on one of the three viewports [16]. In addition to the feed gas flown through the APPJ, 2 sccm CH_4 carried by 400 sccm Ar was injected downstream of the APPJ near the catalyst bed. At this location, the methane and reactive species generated by the APPJ, can interact with each other and with the catalyst through which the gases left the reaction chamber. The quartz tube-to-catalyst distance was fixed at 5 mm for all experiments performed in this work. This distance enabled a relatively large amount of reactive species to arrive at the catalyst surface and allowed a large range of power changes without the plume touching the catalyst and generating arcing. Note that varying the plasma-to-catalyst distance is expected to change certain aspects of the results reported here (see [11]), but this characteristic is not dealt with in this work. The methane and gas products produced from the plasma-catalyst interaction entered a lab-made gas cell with a 15 cm optical path length sealed with two ZnSe windows, where real-time gas phase characterization was performed using an FTIR spectrometer (IRTracer-100, Shimadzu) equipped with a liquid nitrogen-cooled Mercury-Cadmium-Telluride (MCT) detector. All the gas phase characterizations were done at 0.5 cm^{-1} resolution, Happ-Gentzel apodization and with 10 scans averaged to reduce the baseline noise and improve accuracy. Operando DRIFTS measurements were performed to characterize the catalyst surface. In DRIFTS, the infrared beam passes through KBr windows installed on two viewports of the dome and is scattered off the catalyst surface. The IR beam is then reflected by mirrors in the DRIFTS accessory (Praying Mantis, Harrick Scientific) towards the spectrometer detector. IR spectra showed peaks corresponding to CO, CH_n and other oxygenates, and their intensities were analyzed. Details of the DRIFTS setup and characterization can be found in [16].

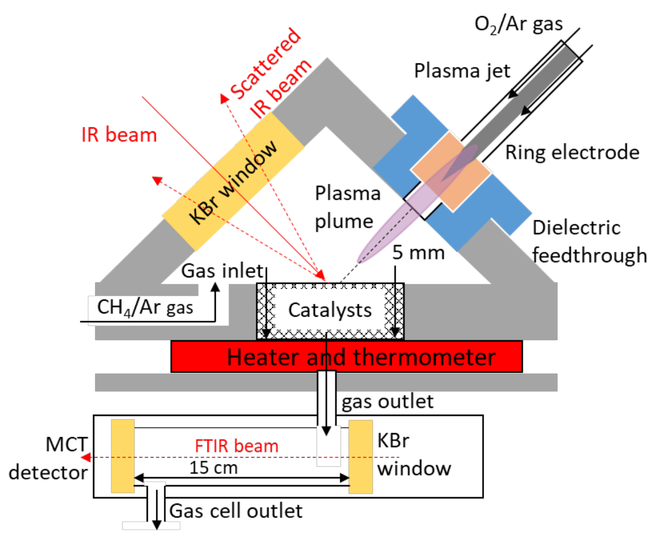

Figure 1. The scheme of the reactor for plasma-catalyst interaction and DRIFTS and downstream FTIR measurements. The figure was modified based on the one shown in [16].

The gas lines were evacuated to 10^{-5} torr before each experiment, and the reaction chamber was purged by Ar flow to eliminate ambient CO_2 and water vapor that cannot be differentiated from the products of the reactions. During the experiments, the plasma power was increased in steps to the highest possible power without arcing. The plasma treatment time was 5 minutes at each power level which is long enough for the reactions to reach steady state. Both measurements with the catalyst bed at 25 ºC and heated to 500 ºC were performed. The catalyst was thermally activated around 360 °C without plasma. However, at this temperature, the thermal catalysis was weak, and the plasma effect still dominated over the thermal effect and the plasma-catalysis synergy effect was weak. At 500 °C, the thermal catalysis plays an important role and can convert a relatively large amount of CH_4 gas. For the high temperature experiments, the catalyst was heated at a rate of 10 ºC/min. When it reached 500 ºC, pure thermal catalytic reactions were first recorded as a baseline before the APPJ was ignited. Temperature-programmed experiments have also been performed to investigate the plasma effect on the activation energy of the reactions. In these experiments, the plasma was either on or off through the entire temperature ramping process.

The plasma-produced reactive species flux was measured at 5 mm from the nozzle, corresponding to the location of the catalyst bed, with MBMS. The sampling occurred through an orifice of 30 μm in a stainless-steel substrate. More details of the measurement procedure can be found in [31, 35]. As the plasma jet was not in direct contact with the catalyst nor the substrate, the species production in the plasma are independent of the material of the sampling substrate.

3. Results

3.1. Real-time downstream gas phase characterization

Typical FTIR spectra obtained for a 0.5% O_2/Ar flow with and without plasma and at a catalyst temperature of 25 °C and 500 °C are shown in figure 2. Due to the large disturbance of water vapor from ambient environment, water, a possible product of the oxidation of methane, was not quantitatively investigated in this work. The other three species, CH_4, CO and CO_2, all show IR absorption features that could be related to their density by Beer's law. It should be stressed that the background spectra were taken after the CH_4 flow was applied, which is why the consumption of CH_4 leads to a negative absorbance.

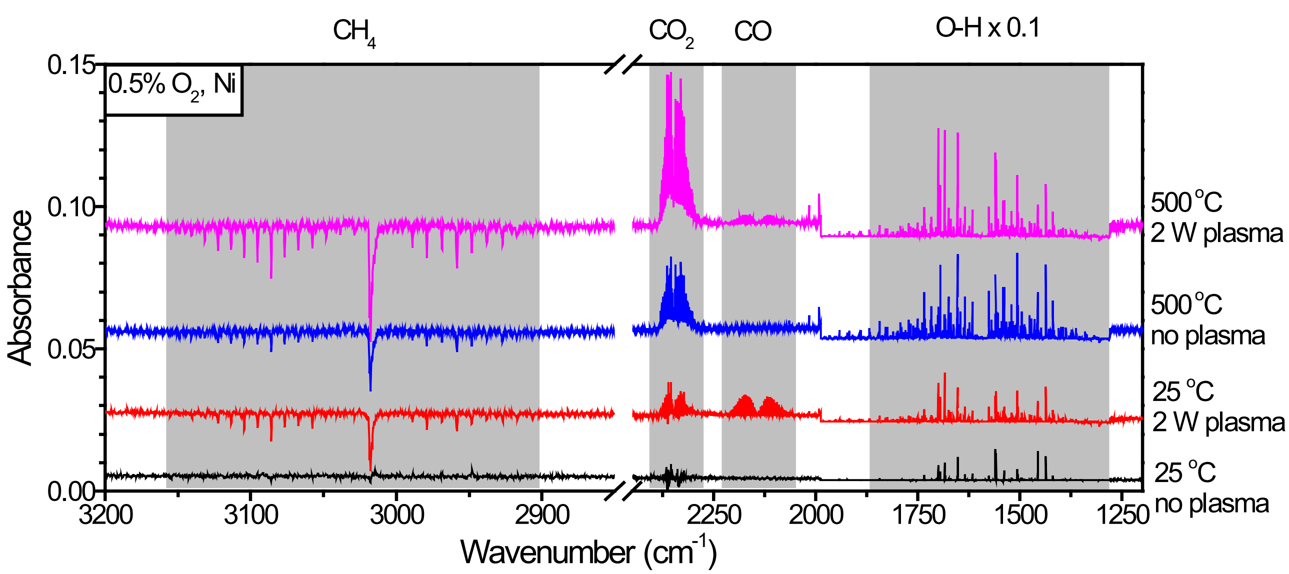

Figure 2. Overview of the gas phase FTIR spectra with a feed gas composition of 0.5% O_2 in 200 sccm Ar with catalyst temperature of 25 °C without plasma (black), 25 °C with plasma (red), 500 °C without plasma (blue), and 500 °C with plasma (purple).

The IR spectrum recorded at 25 °C without plasma (black spectra) has no CH_4 and CO absorption features, consistent with neither CH_4 is consumed, nor CO is generated. Nonetheless some CO_2 features can be observed due to fluctuation in the ambient CO_2 density in the IR beam path, but the average density calculated from those features remains negligible (~10^{13}). When the

APPJ was switched on with the catalyst at 25 ºC (red spectra), CH_4, CO and CO_2 features readily appeared, indicating that the oxidation of CH_4 to both CO and CO_2 was taking place. With the catalyst at 500 ºC without plasma (blue spectra), thermal catalytic reactions did not produce CO gas but the CH_4 was undergoing complete oxidation to CO_2. When the plasma was switched on with catalyst at 500 ºC (purple spectra), a drastic increase of CH_4 consumption and CO_2 generation could be seen, while CO absorption bands have a lower intensity than that at 25 ºC.

The IR absorbance of CH_4, CO and CO_2 were converted to number density (number/cm^3) based on Beer's law, which is shown in the following equation:

$$n = \frac{Abs}{0.4343 * \sigma * l} \qquad (1)$$

In this equation, n is the density of the gas calculated from a certain absorption peak, Abs is the absorbance measured by FTIR at that peak, σ is the attenuation cross section, which is calculated from the HITRAN FTIR database [36], and l is the optical path length of the gas cell which is 15 cm [16]. To calibrate the gas density, a known amount of CH_4, CO or CO_2 was flowed through the gas cell. The measured density was found to be linearly proportional to the real concentration, and a correction factor for each gas was obtained by comparing the real density with the measured density, which was 2.789, 0.46 and 0.19 for CH_4, CO and CO_2, respectively. Details of the gas quantification method can be found in [16].

3.1.1. Variation of plasma power, O_2 flow rate and catalyst temperature

The concentration of consumed CH_4, generated CO and CO_2 at a catalyst temperature of 25 ºC and 500 ºC as a function of the plasma dissipated power is plotted in figure 3. In general, increasing the plasma power can enhance the CH_4 consumption and CO and CO_2 production, which is due to the increase of plasma density, reactive species fluxes and plasma plume length.

Conversely, increasing the O_2 flow rate lowers the CH_4 conversion at the catalyst temperature of 25 ºC, as the reactive species density and plasma plume length are reduced upon the addition of O_2 gas [37]. However, at 500 ºC in the thermal-driven dominant region (low plasma power), the O_2 flow can increase the CH_4 consumption (figure 3b) and CO_2 production (figure 3f) due to the enhancement of thermal reaction. Note that although the error bar for the CO_2 production is relatively large due to the disturbance from the ambient CO_2, figure 3f still shows the increase of CO_2 generation due to the enhanced thermal catalytic reaction induced by the increased O_2 gas at low plasma power region. As for CO, it can only be generated at significant quantities in the presence of plasma for the investigated conditions in this work and the increase in O_2 addition did not enhance CO production even with the catalyst at 500 ºC. In addition, we found that the CH_4 consumption and CO_2 production are enhanced at a catalyst temperature of 500 ºC compared to 25 ºC while the CO production reduces. In this work, the conversion rate of CH_4 to CO and CO_2 is around 90%, which indicates that the formation of other byproducts is not significant. However, less than 10% of the overall methane was oxidized, which was much lower compared to flowing methane through the plasma source [9], because of less direct interaction between the ionizing plasma and the methane.

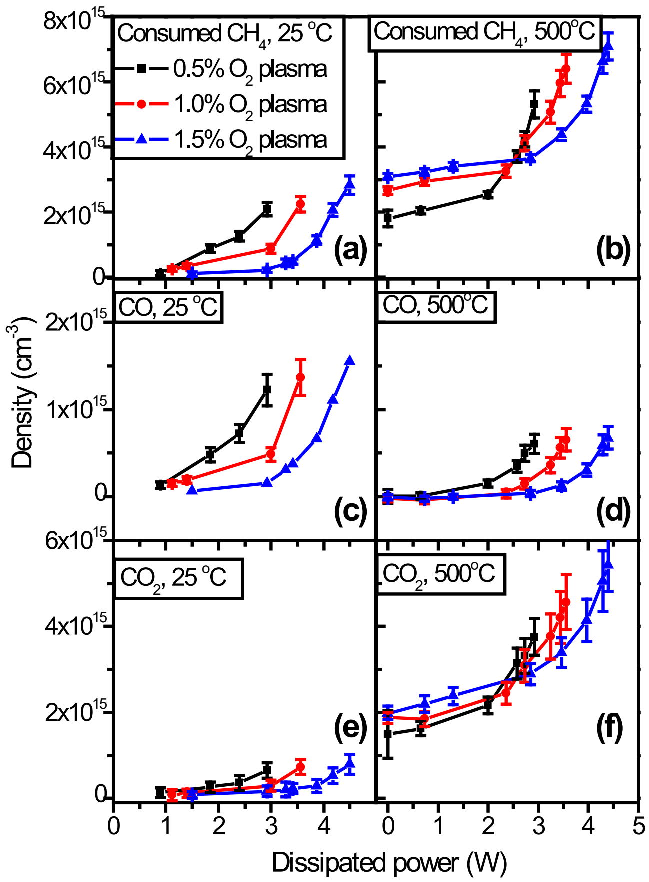

Figure 3. Measured densities of CO, CO_2 and CH_4 under various plasma powers at a catalyst temperature of 25 °C or 500 °C: CH_4 consumption at 25 °C (a) and 500 °C (b), CO production at 25 °C (c) and 500 °C (d), and CO_2 production at 25 °C (e) and 500 °C (f).

3.1.2. Temperature-programmed experiments

To evaluate the effect of plasma on the activation energy, temperature-programmed experiments were performed with and without plasma application. The nickel catalyst was continuously heated from 25 °C to 500 °C at 10 °C/min with 1 W plasma jet. Downstream gas-phase measurements were recorded throughout the entire temperature-ramping process. As shown in figure 4a, the consumption of CH_4 is an activated process that is enhanced with temperature.

Without plasma, the nickel catalyst was activated at 360 ºC, as indicated by the temperature where the consumption of CH_4 started to increase. With 1 W plasma, the activation temperature was lowered to 310 ºC. It is worth noting that the gas temperature of a 1 W plasma was measured to be ~310 K, hence the heating due to the plasma was negligible [38].

As we have seen in figure 3, CO production becomes weaker while the CO_2 production is boosted at a catalyst temperature of 500 ºC than at 25 ºC, one may speculate that CO is oxidized to CO_2 at elevated catalyst temperature. We conducted an experiment to evaluate the temperature evolution of CO and CO_2. The plasma power was set at a relatively high value (3 W) in order to enhance the plasma-catalyst interaction. In figure 4b, the CO curve starts to decline at around 200 ºC, while the CO_2 curve begins to increase at the same temperature. This result clearly demonstrates that CO_2 is favored at high temperature. It is worth noting that the amount of decreased CO cannot compensate for the amount of increased CO_2 since the CO_2 production at high temperature with plasma also includes the thermal catalysis and other synergistic effects that can enhance the reaction. We also found that heating of the catalyst does not cause noticeable change of the plasma properties (shown in figure 9), the oxidation of CO to CO_2 should happen on an activated catalyst surface.

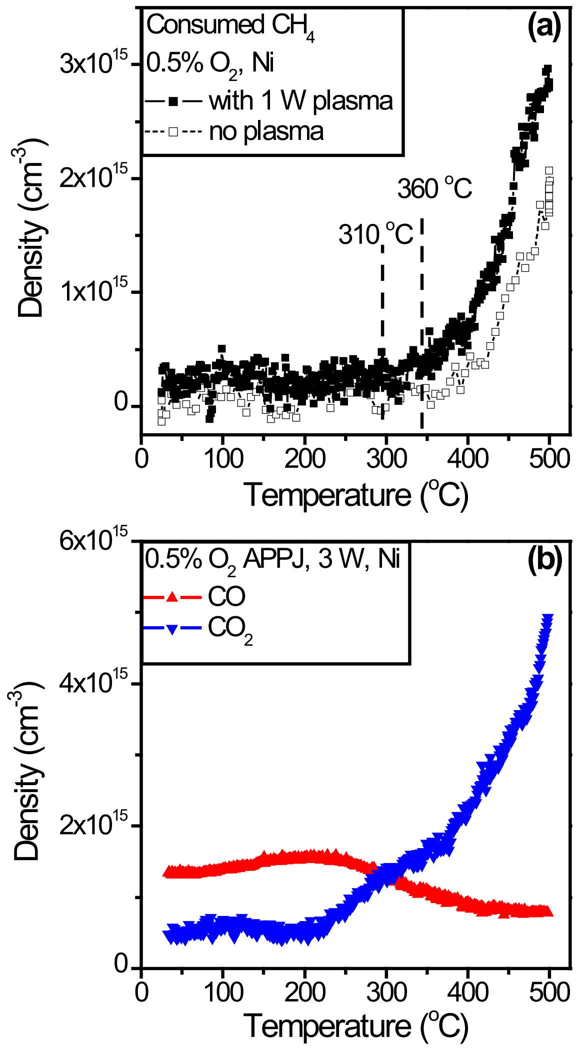

Figure 4. (a) The temperature dependence of CH_4 consumption with and without the 1 W Ar/O_2 plasma. (b) Density profile of CO and CO_2 as a function of temperature using 3 W Ar/O_2 plasma. The catalyst was heated from 25 °C to 500 °C at 10 °C/min.

3.2. Reactive oxygen species

The most dominant ROSs produced by Ar/O_2 APPJ are atomic oxygen, ozone and singlet oxygen, and their density profile measured by MBMS was shown as a function of dissipated plasma power in figure 5. The variation of the atomic O density exhibits a similar trend with plasma power as the consumed CH_4 and produced CO and CO_2 densities do, while O_3 and singlet O_2 do not have similar correlation. We have correlated the fluxes of atomic O and gas phase species from the CH_4 conversion reactions and is discussed in 4.2. For additional information regarding the ROSs produced by the APPJ, the reader can refer to [31, 34].

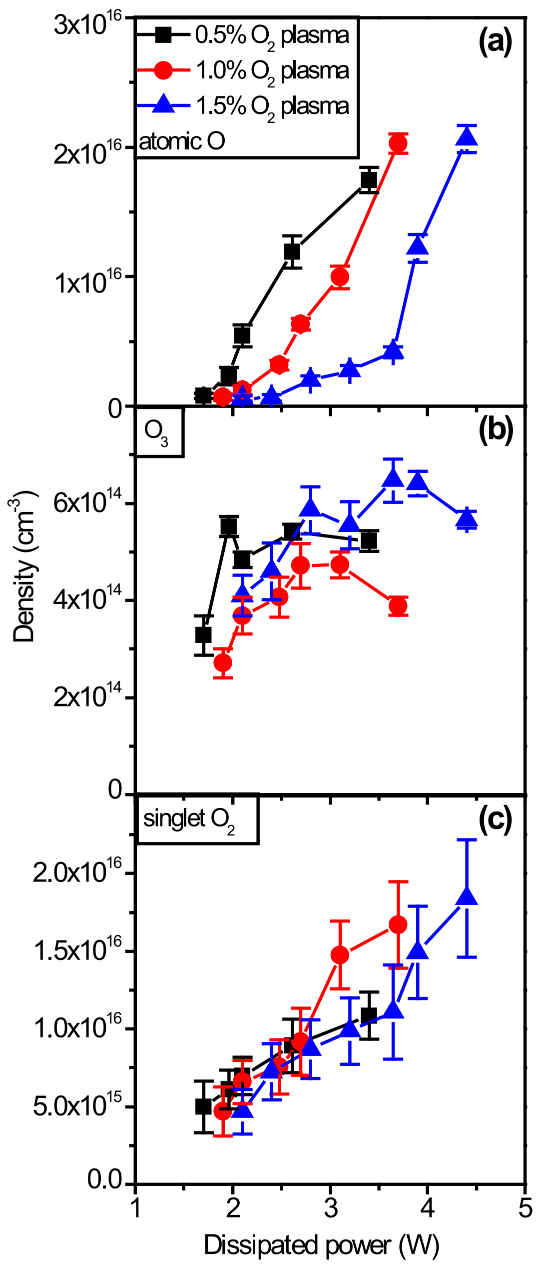

Figure 5. The ROSs densities at a distance of 5 mm from the APPJ nozzle as a function of plasma power [31, 35].

3.3. DRIFTS results

The evolution of surface species on the catalyst was measured in-situ by the DRIFTS cell integrated into the FTIR sample compartment. The experimental conditions and plasma treatment procedure were the same as for the downstream gas phase measurements so that complementary gas phase and surface data could be obtained. The FTIR was set at 4 cm^{-1} resolution, Happ-Gentzel apodization and with 20 scans averaged for the DRIFTS measurements. Background spectra were taken using a pristine catalyst sample. Thus, a positive signal in the DRIFTS measurements indicates the formation of surface species, whereas a negative signal means a loss of surface species. While no quantitative analysis of the DRIFTS measurements were attempted, the changes in relative absorbance in the DRIFTS spectra is still qualitatively related to the abundance of the surface species [39].

Figure 6 shows a selection of DRIFTS spectra for catalysts at 25 °C and 500 °C with or without a 2 W plasma jet with 0.5% O_2. The band observed around 3500 cm^{-1} is associated with hydroxyl groups [40]. The hydroxyls can be derived from either the chemical reactions, or the water vapor residues inside the reactor and gas tubing. CH_4 peaks at 2900 to 3150 cm^{-1} and around 1300 cm^{-1} [41] can be observed. However, these peaks are due to changes in gas phase CH_4 rather than surface-adsorbed CH_4. This was confirmed by DRIFTS measurements after the plasma treatment and flushing of the reactor that led to the immediate disappearance of the CH_4 absorption features, while surface species typically remain on the surface longer and retained their absorption features. Similarly, gas phase absorption can be observed for CO_2 around 2280–2290 cm^{-1} [42, 43]. The origin of these gas phase absorptions was from the IR light going through the gas phase above the catalyst before and after it was scattered on the surface.

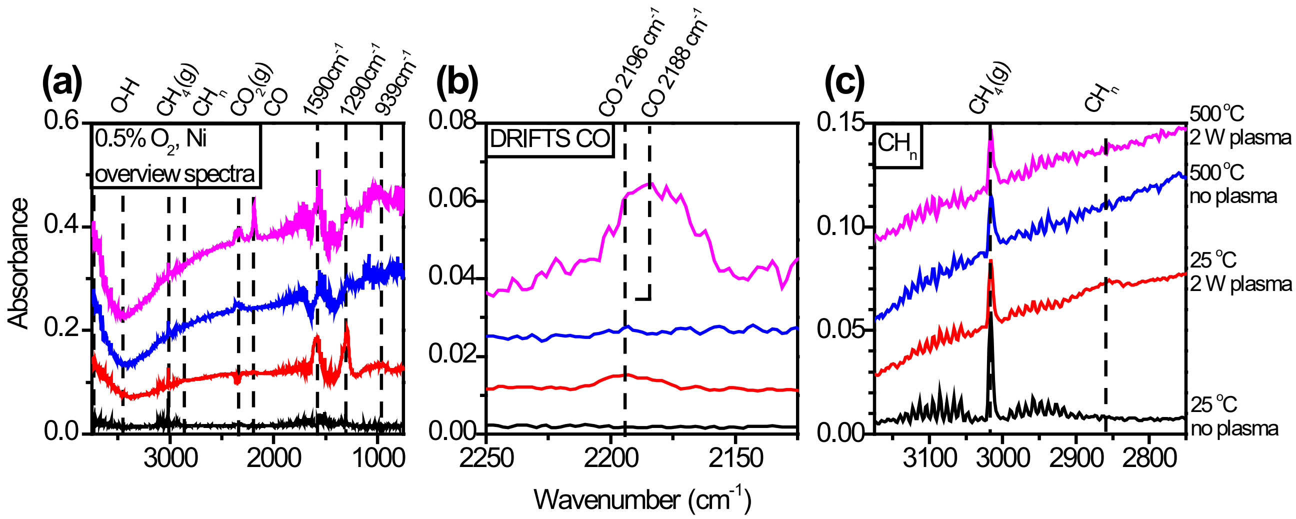

Figure 6. The DRIFTS spectra with or without the 2 W plasma jet with a gas composition of 0.5% O_2 in 200 sccm Ar at a catalyst temperature of 25 °C and 500 °C: 25 °C no plasma (black), 25 °C with plasma (red), 500 °C no plasma (blue), and 500 °C with plasma (purple). (a) An overview of DRIFTS spectra. (b) Magnified spectra of the surface CO. (c) Magnified spectra of the surface CH_n and gas phase CH_4.

For a catalyst sample at 25 °C without plasma, other than O-H and gas phase CH_4 peaks, no other IR peaks are observed. When the 2 W APPJ was applied on the 25 °C catalyst, a surface CO absorbing at 2196 cm^{-1} [11] and surface CH_n absorbing at 2860 cm^{-1} [41, 44] was observed, as shown in figure 6b and 6c by the red spectra. Unfortunately, the IR bands of CH_n (n=1, 2 and 3) overlap in the range of 2800-3100 cm^{-1} in our experiment [45], and unambiguous assignment of the peaks to a specific CH_n species is difficult, thus we refer to the band at 2818–2914 cm^{-1} as CH_n in general. For a catalyst at 500 °C without plasma, no surface CO or CH_n peaks were observed as shown by the blue spectra in figure 6, which is consistent with the gas phase results that no CO and only CO_2 is produced at 500 °C without plasma (figure 2). After the APPJ was switched on at 500 °C, a strong surface CO peak at 2188 cm^{-1} was observed. No surface CH_n was observed at this condition, which is a distinctive difference with the 25 °C catalyst case. In figure 6b, the vibrational frequency of CO shows a blue shift from the gas phase free CO molecule (2143cm^{-1}, figure 2) to surface-adsorbed CO at 25 °C (2196 cm^{-1}) and 500 °C (2188 cm^{-1}). This is likely due to the oxidation state of nickel and will be discussed in 4.4.

The other absorption features present in the DRIFTS spectra at 1590 cm^{-1}, 1290 cm^{-1}, and 939 cm^{-1} can be assigned to carboxylate [41, 46], carbonate [47], and superoxo or nickel oxide [48], respectively. The unambiguous assignment of the peaks between 750–1800 cm^{-1} is hard, as many species, such as carbonate, carboxylate, hydroxyl, etc. with overlapping absorption bands are located in this range. Additionally, the absorbance of these species seems independent of the plasma power, as shown in figure 7. In the scope of this work, it is possible that those species act as spectator species or mild intermediates that do not play a key role in the reactions, as discussed by Demoulin et al. [42] and Meunier et al. [49] in their work. Further investigation of those species is outside the scope of this work.

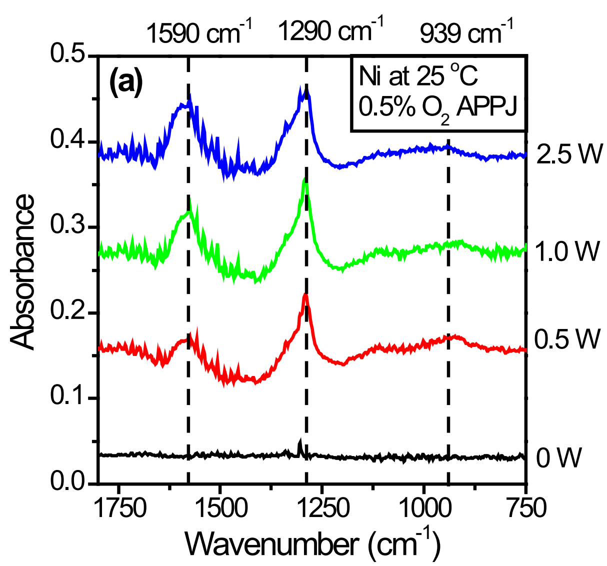

Figure 7. DRIFTS spectra in the region of 750-1800 cm^{-1} at the catalyst temperature of 25 ºC. The APPJ feed gas was 0.5% O_2 in 200 sccm Ar, and different powers were selected. Three main absorption features from surface species at 1590, 1290 and 939 cm^{-1} might be assigned to carboxylate, carbonate and O_2^- ions or nickel oxide, respectively.

4. Discussion

4.1. Effects of O_2 additives on decomposing CH_4

Figure 8a shows that increasing the O_2 admixture to Ar/O_2 feed gas decreases the consumption of CH_4 at 25 ºC. The addition of O_2 to the plasma source leads to the quenching of high-energy electrons, metastable species and reactive oxygen species [37, 50-52], resulting in the decrease of plasma-induced reactivity. The plasma plume length also decreases significantly upon increasing O_2 addition [52]. The correlation between plume length and conversion has two origins: the stronger mixing of the surrounding CH_4 with the ionizing plasma in the case of the larger plume length or the distance short-lived radicals that are rapidly decaying afterglow have to travel. In addition, the lifetime of, for instance, the O radical is strongly impacted by the O_2 concentration as its main destruction pathway is through the recombination with O_2 forming O_3 in a three body reaction [32]. Hence, the O_2 concentration could drastically impact O flux to the catalytic surface and reduce the CH_4 conversion.

At a catalyst temperatures of 500 ºC, an increased amount of O_2 can promote the consumption of CH_4 in thermal-driven catalytic reactions as shown in figure 8b [53]. This process seems to favor CH_4 to CO_2 conversion. This conclusion remains valid in plasma catalysis with low plasma power, where the dominant reaction is still the thermal-driven catalytic reaction. With increasing plasma power, however, the plasma-induced effects become more pronounced and a similar reduction in CH_4 conversion with increasing O_2 addition occurs. The transition point between these two different trends is 2.5 W. At this power, CH_4 conversion is independent of the amount of O_2 added to the feed gas.

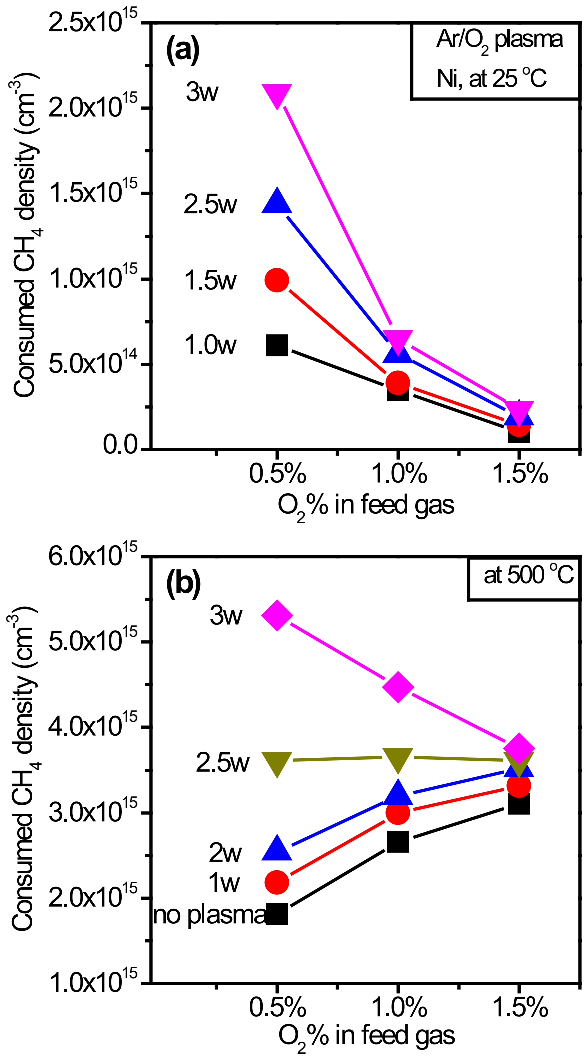

Figure 8. CH_4 consumption for different O_2 amounts in the feed gas at different plasma powers at a catalyst temperature of 25 ºC (a) and 500 ºC (b). As a reference, no plasma conversions have also been included. The data are extracted from figure 3.

4.2. Role of atomic O

4.2.1. Validity of using MBMS fluxes to correlate with conversion

Before looking in more depth to correlations between plasma-produced ROSs and CH_4 conversation, it is crucial to assess whether heating of the catalyst bed impacts plasma conversion. To this end, we replaced the catalyst with kieselguhr powders treated by plasma and assessed the CH_4 conversion at a kieselguhr powder temperature of 25 ºC and 500 ºC without the presence of a metal catalyst as shown in figure 9. No significant difference in CH_4 conversion was observed confirming that the heating of the catalyst bed to 500 ºC has a negligible effect on the methane conversion.

As the catalyst particles were loosely packed in the holder, the effluent of the plasma jet could easily flow through the catalyst holder without much flow resistivity in the experiments. The convection timescale over a distance of 1 mm when approaching the catalyst bed is estimated to be ~1.7 ms, based on the gas velocity entering the catalyst holder. When the catalyst temperature increases from 25°C to 500°C, the convective transport of reactive species to the catalyst holder is not impacted significantly. This is because the timescale of thermal diffusion is estimated to be on the order of ~45 ms over a distance of 1 mm (based on l^2/α, l is the characteristic length and α is the thermal diffusivity of Argon 2.2×10^{-5} m^2 s^{-1}), which is much longer than the corresponding convection timescale (~1.7 ms). Therefore, the convection is more dominant over the heat diffusion and there is negligible temperature gradient in the upstream gas phase before the catalyst holder. Hence the plasma produced reactive species fluxes measured at 25°C are representative for both the catalyst operating at 25°C and 500°C. Note however, that this estimate implies that the thermal gradients occur in the catalytic bed and the given temperatures should be interpreted as holder temperatures during the application of the gas flow.

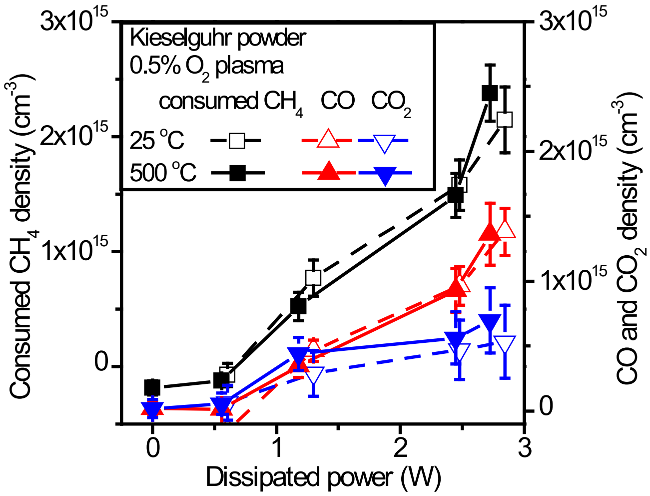

Figure 9. CH_4 density as a function of plasma power with kieselguhr powder instead of catalyst at a temperature of 25 ºC and 500 ºC.

4.2.2. Correlation between CH_4 conversion and atomic O flux

To evaluate the effect of the ROSs produced in the plasma, we converted the measured density (cm^{-3}) to flux ($cm^{-2}s^{-1}$) on the catalyst surface at a distance of 5 mm from the quartz tube. As the gases flow through the catalyst bed (and in the case of the MBMS similarly gas suction into the sample orifice occurs) the catalyst surface is not a stagnation zone and the flux can be estimated from the local gas velocity and density as the species are convectively transported into the catalytic bed.

$$\Gamma = \frac{\rho Q}{A} \qquad (2)$$

Here Γ is the average particle flux ($cm^{-2}s^{-1}$), ρ is the gas density (cm^{-3}) which can be measured by FTIR for CH_4, CO and CO_2, and by MBMS for ROSs, Q is the volumetric flow rate (cm^3s^{-1}), A is the catalyst bed cross section (cm^2). While we recognize that in this system concentration gradients will be present due to mixing of the feed gas through the jet and gas added in the chamber, a first order estimate of the gas velocity at the catalytic bed can be obtained by expressing mass conservation of the gas flow through the system.

By correlating the ROSs and the consumed CH_4, and produced CO and CO_2 fluxes, we found that atomic O flux exhibits a linear correlation with the fluxes of consumed CH_4 and produced CO and CO_2, as shown in figure 10. However, the other two ROSs, singlet oxygen and ozone, do not show any obvious correlation. The flux of the consumed CH_4, produced CO and CO_2 is proportional to the atomic O flux delivery to the catalytic bed, and the curves coincide for all O_2 flow rates at a catalyst temperature of 25 ºC. As the ion flux and UV flux are very small for these jet conditions [50, 54], these observations are consistent with the hypothesis that atomic O is the key reactive species that contributes to the reaction. Luan et al. [55] studied polymer etching using a similar APPJ, and they found that the etching depth of the polymers mirrors the flux of atomic O produced from the APPJ, and a similar proportional relationship between the etching depth and atomic O flux was established. They concluded that the atomic O initiates and directly participates in the polymer etch [55] which was confirmed by a detailed quantitative analysis involving a broader range of radical species in [56]. In addition, at a catalyst temperature of 500 ºC, the enhancement of the O_2 flow on thermal conversion of CH_4 to CO_2 is reflected in figure 10, indicating that the thermal catalytic reaction utilizes O_2 gas to oxidize CH_4.

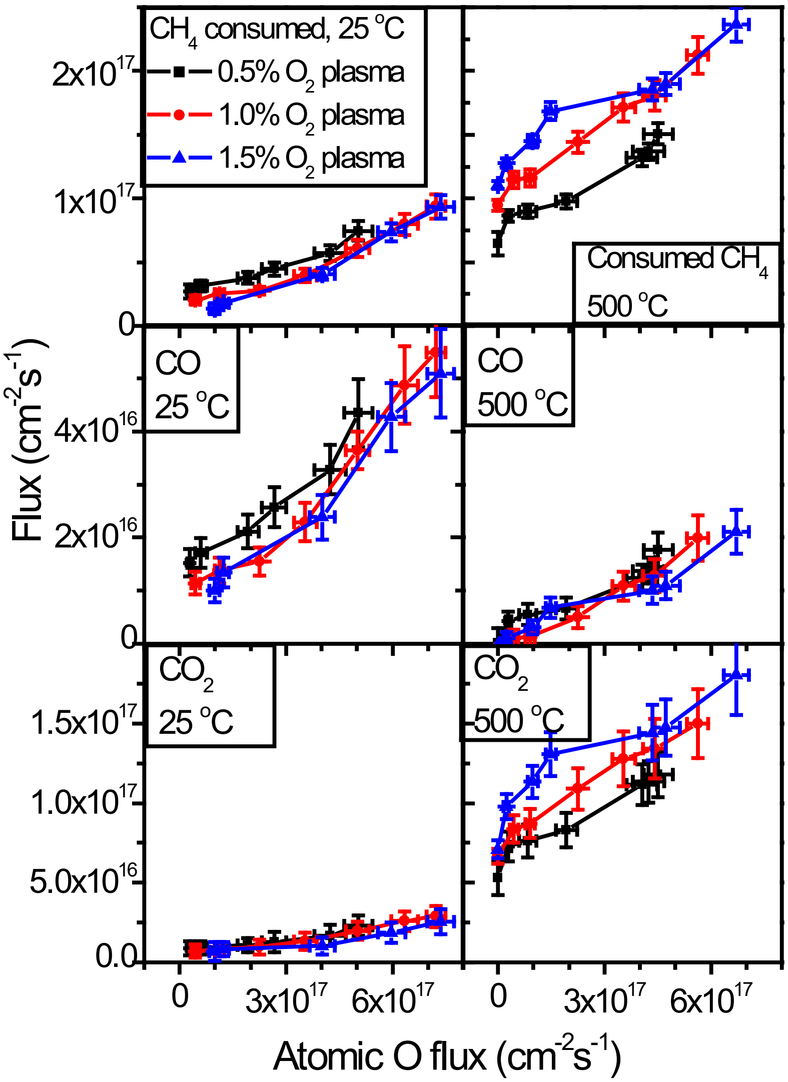

Figure 10. Correlation between the fluxes of consumed CH_4, produced CO and CO_2 and atomic O at the catalyst temperature of 25 °C (a) and 500 °C (b). The concentration of CH_4, CO and CO_2 was extracted from figure 3, and that of atomic O was extracted from figure 5. The fluxes of the gases and atomic O were calculated based on Eq. (2).

4.3. Apparent activation energy and synergistic effect

Based on the temperature dependence profile of CH_4 consumption in figure 4a, the apparent activation energy can be calculated through the rate equation and Arrhenius equation:

$$r = K[\mathrm{CH_4}]^a[\mathrm{O_2}]^b \qquad (3)$$

$$K = A \cdot e^{-\frac{E_a}{RT}} \qquad (4)$$

Here r is the CH_4 consumption rate, which is calculated by multiplying the concentration of consumed CH_4 by the total flow rate, K is the reaction rate coefficient, a and b represent the reaction order for CH_4 and O_2 respectively, E_a is the apparent activation energy, and T is the temperature of the reaction. By combining the two equations, the apparent activation energy can be extracted from the slope of CH_4 consumption rate vs. $1/T$.

$$\ln(r) = \ln(a) + a \cdot \ln[\mathrm{CH_4}] + b \cdot \ln[\mathrm{O_2}] - \frac{E_a}{R}\frac{1}{T} \qquad (5)$$

The log of the reaction rate is linearly proportional to $1/T$ with $-E_a/R$ as the slope. Figure 11 is the log of CH_4 consumption rate as a function of $1000/T$. The apparent activation energy is calculated to be 81.86 kJ/mol (0.85 eV) for the thermal catalytic reaction, and 47.86 kJ/mol (0.50 eV) for the plasma-enhanced catalysis reaction, based on the linear fit of the Arrhenius plot as shown by the dashed (no plasma) and solid (with 1 W plasma) lines in figure 11. A decrease in apparent activation energy of over 40% is observed. Geng et al. investigated the methane catalytic combustion over a Cu catalyst, and the apparent E_a was found to be around 100 kJ/mol, depending on the O_2/CH_4 ratio [57]. The discrepancy of measured apparent E_a between their work and ours could be due to the difference of the setup as well as the catalyst used. Unfortunately, we did not find any literature that includes the calculation of the apparent E_a for the oxidation of CH_4 by Ar/O_2 plasma.

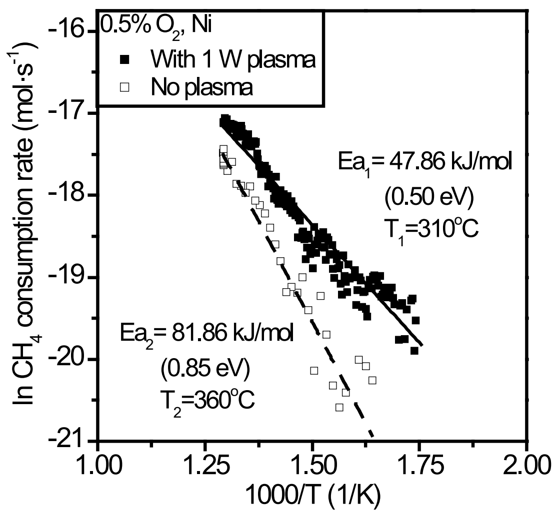

Figure 11. The Arrhenius plot of CH_4 consumption with and without the 1 W O_2/Ar plasma. The data was calculated from figure 4a based on Eqs. (3)–(5).

The plasma can dissociate CH_4 and O_2 to reactive intermediates, such as CH_n for CH_4 (see supplementary material for the discussion of CH_4 dissociation by plasma-produced species) and atomic O for O_2. The plasma can also generate vibrationally excited methane (CH_{4_vib}) which can be dissociated on active catalyst sites with less energy input [58], although this is less likely in the present study as the CH_4 is not fed through the ionizing plasma. The contribution of the plasma lowers the apparent activation energy required to break down the strong chemical bonds that usually require high temperatures [58]. At the catalyst temperature of 500 °C with the APPJ, more reactive species participate in the chemical reactions on the surface than without plasma, which contributes to the synergistic effect in plasma catalysis. As can be seen in figure 12, the catalytic reaction with 1.0% O_2 plasma at 500 °C consumes more CH_4 (31% higher using 3.5 W APPJ) than is consumed if one combines the separate reactions of plasma at 25 °C (pure plasma effect, catalyst was not active) and pure thermal catalysis at 500 °C (no plasma). The sum of CO and CO_2 products using the 1.0% O_2 APPJ at 500 ºC catalyst temperature is also higher than the sum of the separate reactions (32% higher using 3.5 W APPJ). Therefore, a synergy of about 30% can be observed in our system. Nonetheless, the temperature increase at the catalyst bed can extend the lifetime of the O radical as the dominant recombination reaction is highly sensitive to temperature [32]. However, the influence of the increased O radical lifetime on the CH_4 conversion at elevated catalyst temperature is out of the scope of this paper and will not be discussed in this work.

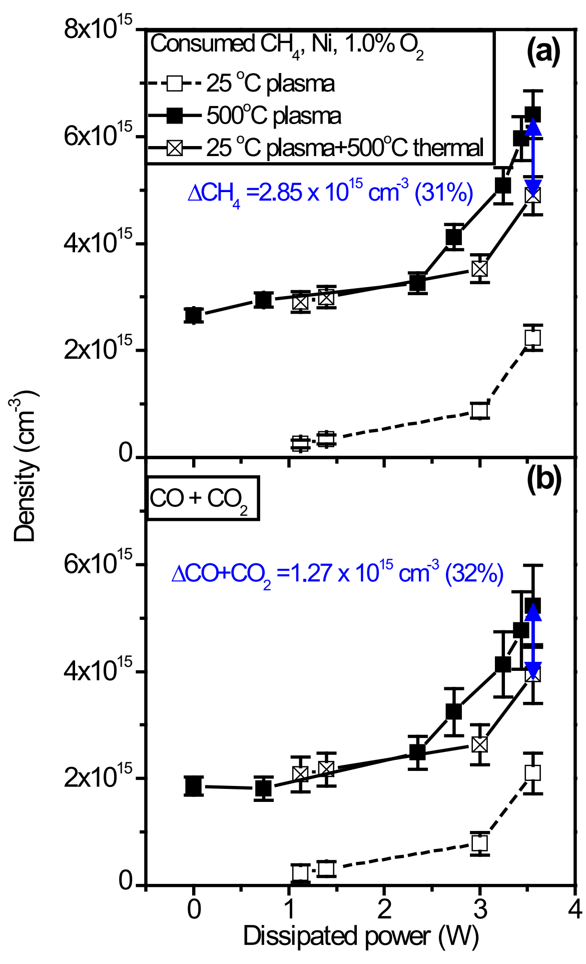

Figure 12. Comparison of plasma catalysis at 500 ºC using 1.0% O_2 in an APPJ with the sum of using an APPJ at 25 ºC and pure thermal catalytic reaction at 500 ºC. Plasma catalysis at 500 ºC (a) consumes

more CH_4 and (b) generates more products (sum of CO and CO_2) than the combination of the other two cases.

4.4. Changes of CO vibrational frequency

One important observation is that the CO IR vibrational frequency shifts from that seen for the CO molecule in the gas phase when a surface-adsorbed species is studied. As shown in figure 13, the free gas CO measured by downstream FTIR has absorbance bands centered at a wavenumber of 2143 cm^{-1}, in agreement with literature [36]. The surface-adsorbed CO measured by DRIFTS at 25 °C catalyst temperature has an absorbance blue shifted by 53 cm^{-1} from the free gas CO frequency. This phenomenon is consistent with simulations by Politzer et al [59]. Politzer et al. attributed the frequency increase of surface-adsorbed CO to the net transfer of charge from the carbon to Ni. Upon the formation of Ni-CO structure, CO could transfer its σ electrons to the Ni surface, while gaining antibonding $2\pi^*$ electrons from the Ni surface [60]. The loss of the σ electrons is larger than the gain of the antibonding $2\pi^*$ electrons if the CO is bonded to positively charged Ni ions, for instance, in nickel oxide, resulting in a stronger C-O bond and giving rise to a higher vibrational frequency. Spectroscopic studies of surface-adsorbed CO also showed that CO bonded to oxide surfaces displays a blue shift from its free gas component [61-63]. Lu et al. found a shift of surface-adsorbed CO bands to higher wavenumber, and they explained such phenomenon by the decrease of electron density on platinum, which was caused by the attraction of electrons from surface oxygen species [63].

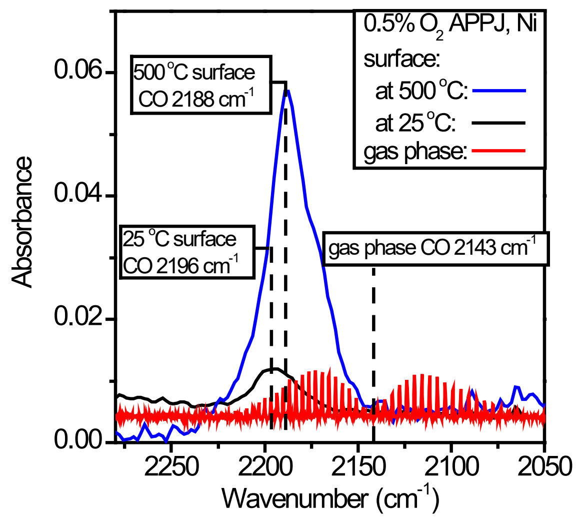

Figure 13. IR spectra of gas phase CO (red) and surface CO at 25 °C (black) and 500 °C (blue). The surface CO exhibits a blue shift from the gas CO (2143 cm^{-1}). The surface CO at catalyst temperature of 500 °C shows a red shift from that at 25 °C.

The catalyst temperature also plays a role in determining the IR frequency of surface CO. When the catalyst temperature goes up to 500 °C, the surface CO shows a wavenumber at 2188 cm^{-1}, which still exhibits a blue shift from the gas phase CO, but the frequency is slightly lower than that of the surface CO at a catalyst temperature of 25 °C. According to the work described in [64], CH_4 could interact with the lattice O in the catalyst to form CO_2. Replenishing lattice O may not be fast enough, and thus a relatively more reduced nickel catalyst can be produced at 500 °C than at 25 °C. The extent of charge transfer increases with the positive charge of the Ni ions [59]. At 500 °C, due to loss of surface oxygen, the nickel ions have fewer positive charges on average than for a 25 °C catalyst. Subsequently, less charge transfer between the surface-adsorbed CO and nickel catalyst takes place at 500 °C, and the blue shift of the CO vibrational frequency at the catalyst temperature of 500 °C would be more moderate than that at 25 °C.

4.5. Important correlations and possible mechanisms of plasma–assisted catalytic reactions for the Ar/CH_4/O_2 system

4.5.1. Analysis of gas phase and surface species with varying plasma power and catalyst temperature

In order to understand the mechanism of the plasma catalysis reactions in our system, we have compared the downstream gas phase measurements with the in-situ surface DRIFTS measurements. The gas phase CO and CO_2 data can be directly extracted from figure 3 and is shown on the right y-axis in figure 14. Qualitative analysis of surface CO and CH_n from the DRIFTS data was processed and shown on the left y-axis in figure 14. The absence of surface CO, surface CH_n and gas phase CO in thermal catalytic reactions in our system (shown as 0 W dissipated power in figure 14b) indicates that the gas phase CH_4 is oxidized to CO_2, possibly by surface O derived from the breakdown of surface-adsorbed O_2 over active catalyst-sites, as also suggested by Hu et al. [27, 64, 65]. By using transient response methods, Hu et al. demonstrated that the gas CH_4 can directly react with surface-adsorbed oxygen to produce CO_2 and suggested that this process possibly follows an Eley-Rideal mechanism [64]. Dissanayake et al. used XPS to analyze the unreduced nickel catalyst surface and did not detect carbon formation on the surface at 500 ºC, and they also did not observe the formation of gas CO at 500 ºC [22].

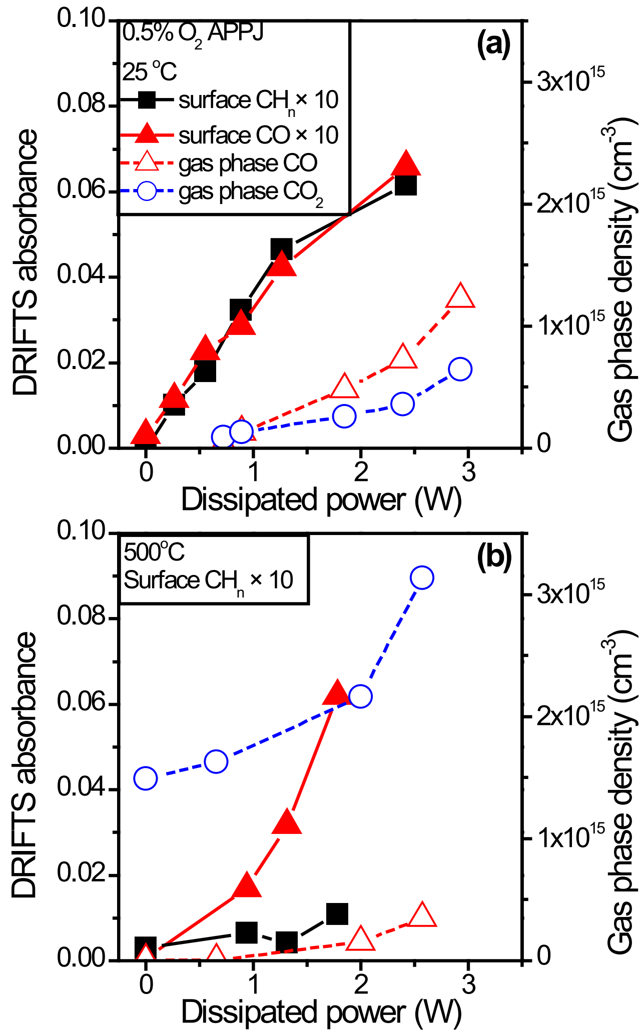

Figure 14. Surface CH_n and CO absorbance, and gas phase CO and CO_2 densities as a function of plasma power at a catalyst temperature of 25 °C (a) and 500 °C (b). The absorbance of surface CO and CH_n at 25 °C and CH_n at 500 °C was multiplied by a factor of 10 for a clearer comparison.

In figure 14a, it is shown that at 25 °C the surface CO follows the trend of surface CH_n with plasma power. This tight correlation indicates that the surface CH_n is connected with the formation of surface CO. The CH_4 can be decomposed by high-energy plasma-produced species and dehydrogenation to CH_n, which is adsorbed on the surface and then oxidized by atomic O to CO and CO_2. Alternatively, the plasma also may produce vibrationally excited CH_4* which can adsorb on the surface as CH_n [58]. Although the reaction is taking place at the surface at 25 ºC as confirmed by the detected surface species, gas phase products can also be generated from the oxidation of adsorbed CH_n on other surfaces by atomic O produced from the APPJ for situations without catalyst and just support. Additionally, we cannot rule out the gas phase formation of CO by direct interactions involving no catalyst site. However, we consider these to be minor reactions and they are not discussed in this work. Knoll et al. [16] demonstrated that the orifice-to-surface distance plays an important role on the acquired results even at a catalyst temperature of 25 ºC, and the plasma impacts are much greater for short orifice-to-surface distances. The reason presented is the short lifetime of O atoms which limits the flux of species that can reach the surface, and the surface reactions will mirror the amount of reactive species that arrive at the surface.

When the catalyst temperature was increased to 500 ºC, we observed very little absorbance due to surface CH_n, while a ten-fold increase of surface CO absorbance was seen as compared to the situation with the catalyst temperature of 25 ºC as plasma power was increased (see figure 14b). The large amount of surface CO species observed at 500 ºC catalyst temperature is contrary to the temperature characteristics of direct adsorption of CO from the gas phase which should become weaker as temperature increases [66, 67]. This suggests that a fast surface CO production reaction should exist on the activated catalyst surface for plasma operating conditions. We postulate that the surface CO species is derived from the rapid oxidization of surface CH_n at 500 ºC driven by incident plasma-produced O, and possibly due to plasma-induced stimulation of interaction with NiO sites. Additionally, thermally driven oxidation of CH_n by surface-adsorbed O_2 takes place at 500 ºC. The oxygen-related consumption of CH_n on an activated catalyst surface is so rapid that its density remains very low, while the surface CO density is high. This is consistent with the dominance of CO_2 gas production over CO gas production at this condition since surface CO can be further oxidized to CO_2 due to the activated catalyst, whereas at 25 ºC such oxidation is less likely to occur. At 500 ºC, the transformation of CH_4 to surface CH_n might be the rate-determining step of the production of CO and CO_2, since the low surface CH_n density limits the reaction rate and the subsequent oxidation proceeds much faster. Nozaki et al. investigated methane steam reforming in a hybrid barrier discharge-catalyst (Ni/Al_2O_3) reactor, and they found that the dehydrogenation of methane is the rate-determining step [3]. The activation of CH_4 to CH_n can be enhanced by directly flowing CH_4 through the APPJ, thus a much higher reaction rate can be achieved. We have investigated such APPJ gas configurations and our observations are consistent with enhanced CH_4 reactivity and greater rates of CO and CO_2 production. We will report our results in the future. At a catalyst temperature of 500 ºC, synergy effects can be observed (as shown in figure 12), since the surface CH_n or vibrationally excited CH_4 [58] can be more easily decomposed to hydrocarbons with lower H content on the active catalyst sites, and the ROSs produced from the APPJ can enhance the thermal reaction as well. The plasma catalytic reactions at 500 ºC include all the reactions discussed for a catalyst temperature of 25 ºC with plasma, along with enhanced thermal catalytic reactions and possible enhancement effects due to plasma-surface interactions. These reactions contribute to the higher conversion rate, lower apparent activation energy and initiating temperature, and synergistic effect of plasma catalysis.

4.5.2. A possible picture of important surface reactions

Based on the discussion in section 4.5.1, we have attempted to bring the data together in first simplified models to explain possible reaction processes for different conditions examined here. This is shown in figure 15. It should be noted that while these processes are consistent with the observations, they are also speculative since further characterization is required, e.g. on the state of the catalyst itself and the extent of plasma-induced gas phase reaction. Nevertheless, we offer this simplified schematic summary of possible processes since this may be helpful in terms of articulating further research questions that may shed light on the unknown mechanisms in plasma catalysis.

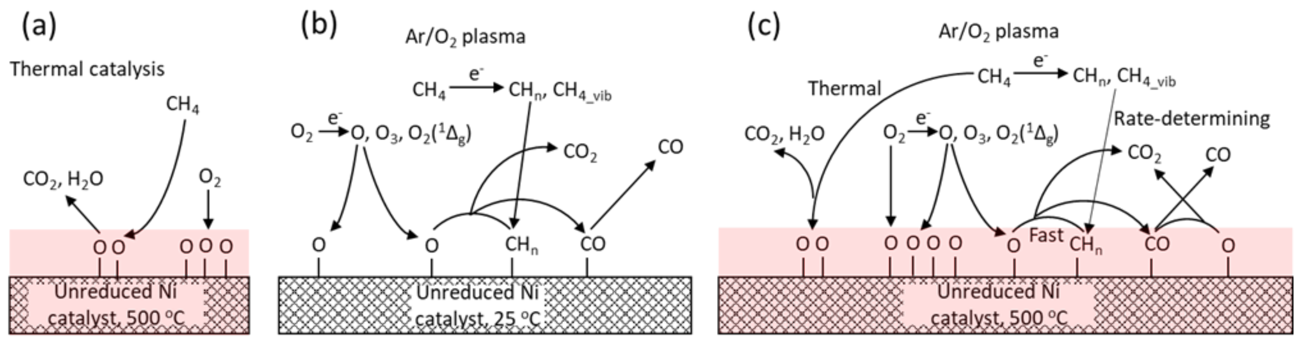

Figure 15. (a) Proposed thermal catalysis processes at a catalyst temperature of 500 °C for CH_4/O_2 system. CH_4 reacts with surface oxygen to produce CO_2 [22, 27, 64]. (b) Scheme of the plasma-assisted oxidation of CH_4 at a catalyst temperature of 25 °C, consistent with observations. O_2 (directly) and CH_4 (only by interaction with the plasma plume) are excited by plasma. Surface-adsorbed CH_n species can be oxidized by atomic O to CO and CO_2. The latter may involve adsorbed oxygen. The catalyst is inactive in this case, and little formation of NiO takes place without the influence of plasma. (c) Scheme of the plasma catalysis reaction at a catalyst temperature of 500 °C. Spontaneous interaction of O_2 with the Ni catalyst produces NiO. Surface CH_n is rapidly oxidized to CO and CO_2 by surface-adsorbed O on the activated catalyst. In addition, CO can also be further oxidized to CO_2 at an elevated catalyst temperature, as illustrated in figure 4b.

5. Conclusions

A non-thermal APPJ using different Ar/O_2 flows has been used to study plasma-catalyst interactions during oxidation of methane over a nickel catalyst at different temperatures. Analysis of FTIR-based gas phase and surface reactive-species measurements has shed light on the mechanisms of plasma-assisted catalytic CH_4 conversion. CH_4, CO and CO_2 were characterized downstream of the catalyst bed by FTIR, and the catalyst surface was analyzed by operando DRIFTS under the same conditions. By varying the O_2 flow rate through the APPJ source at catalyst temperatures of both 25 ºC and 500 ºC, we found that the O_2 addition in the plasma can suppress the plasma-enabled CH_4 conversion (low catalyst temperature), while enhancing the thermal catalytic reaction (high catalyst temperature). The fact that plasma density increases both O atom generation and excitation of methane is consistent with the strong plasma power dependence observed. Reactive species in the plasma effluent analyzed by MBMS using an identical APPJ were correlated with the gas phase conversion and surface species measurements. By correlating the quantified ROSs fluxes (obtained by the characterization of the plasma effluent using MBMS) with the measured rates of CH_4 consumption and CO and CO_2 production, we found that the fluxes of the converted CH_4 and the CO and CO_2 products correlated best with the variation of the atomic O fluxes. This indicates that plasma-produced atomic oxygen is a key species responsible for the oxidation of CH_4 to CO and CO_2 for the experimental configuration used in the present work. The work presented here demonstrates a compelling correlation of the products from plasma-catalytic reactions with the incident reactive species flux from the plasma effluent for specific experimental conditions used here. Catalyst heating experiments showed that the apparent activation energy can be lowered by 40% with the assistance of the APPJ. DRIFTS spectra obtained on the catalyst revealed information on surface species. A blue shift of the CO vibrational frequency from the gas phase CO to surface CO was observed. A possible explanation of this is the change of the oxidation state of the nickel catalyst. We also found the abundance of surface CO followed that of surface CH_n species at a catalyst temperature of 25 °C. This indicates that CH_n is adsorbed and then transformed into CO. It also suggests that the excitation of CH_4 to form CH_n on the catalyst surface mirrors the flux of O atoms to the catalyst surface, but that oxidation to CO is limited by the arrival rate of O atoms. The lack of appreciable surface CH_n along with increased surface CO at a catalyst temperature of 500 °C can be explained by additional thermal oxidation and indicates that the decomposition of CH_4 to CH_n may be the rate-determining step at elevated catalyst temperature. Based on the observation, a conceptual model for thermal catalysis, plasma-induced reaction at 25 °C and plasma catalysis at 500 °C has been built to understand the plasma-catalyst interaction.

6. Supplemental material

Due to the very large dissociation energy of CH_4, only a few reactive species produced by the plasma will dissociate CH_4 in the gas-phase at sufficiently high rates to be impactful, including energetic electrons and O atoms. In this study the CH_4 is not fed through the ionized plasma jet, the entrainment of CH_4 into the plasma jet effluent is necessary for gas phase dissociation. To assess the importance of gas phase CH_4 dissociation in the afterglow region of APPJ, a simple estimation was performed to evaluate the possible roles of electrons and O atoms based on rate coefficients of the following CH_4 dissociation reactions:

$$e^- + CH_4 \rightarrow e^- + CH_3 + H,\ k_1 = f(T_e) \tag{R1}$$

$$O + CH_4 \rightarrow CH_3 + OH,\ k_2 = 2.26\times10^{-12}\ (T/298)^{2.20}\exp(-3819.84/T)\ \mathrm{cm^3\ s^{-1}} \tag{R2}$$

The role of other dominant reactive species such as $O_2(a^1\Delta_g)$ and O_3 can be ruled out due to their low energies, although recombination of O_3 can lead to the formation of O in the plasma effluent. The threshold energy of R1 is ~10 eV according to the cross-section data from [68]. Assuming the electron temperature of 2 eV, consistent with the measurements in [37] using a similar plasma jet in the Ar+0.5% O_2 + 0.33% CH_4 gas composition, the non-Maxwellian properties of electron energy distribution function (EEDF) deplete the high energy electrons (>10 eV), and an upper limit of k_1 is calculated to be 5×10^{-14} cm^3 s^{-1} with BOLSIG+ (12/2019) [69] using the PHELPS database from LXCat [70]. On the other hand, the rate coefficient of the competing reaction k_2 at 350 K (gas temperature in the jet effluents) is calculated to be 5.9×10^{-17} cm^3/s. Note that CH_4 mostly diffuses into the jet effluent instead of the active plasma region, particularly for larger O_2 concentrations with shorter plasma plume length. At the tip of the plasma plume, the O density will be in excess of 2×10^{16} cm^{-3} and the electron density will be ~ 10^{12} cm^3/s. This suggests the dissociation of CH_4 by O density is most likely more effective than electron-induced CH_4 dissociation. This might suggest significantly different conditions compared to a DBD system where transient higher electron temperatures are obtained and CH_4 dissociation has been attributed to electron-induced reactions [58]. Nevertheless, the characteristic timescale of these reactions remains slow for the investigated plasma conditions to fully explain the gas phase conversion and other processes involving excited state molecules, such as $O(^1D)$, cannot be excluded. A further analysis requires detailed modeling which is out of scope of this work.

7. Acknowledgments

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