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A design of a fixed bed plasma DRIFTS cell for studying the NTP-assisted heterogeneously catalysed reactions

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A newly developed diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS) cell for the *in-situ* study of non-thermal plasma (NTP)-assisted heterogeneously catalysed reactions is presented and evaluated using methane oxidation over a Pd/Al₂O₃ catalyst. By using the new fixed bed plasma DRIFTS cell coupled with mass spectrometry, the NTP discharge is generated inside the catalyst bed and allows simultaneous, *in-situ* DRIFTS analysis to be undertaken. The spectroscopy has revealed that the formation of surface species, e.g. formate and carbonate, is significantly influenced by NTP generation under methane oxidation conditions at different voltages when comparing with the conventionally thermal activation. During the NTP-DRIFTS-MS measurements, it is also found that there is no signal interference between IR beam and plasma plume, making this a viable DRIFTS system for studying the plasma catalysis.

1. Introduction

Non-thermal plasma (NTP) assisted catalytic processes have been extensively studied due to the interest in applying them in industrial, environmental and medical fields of research^{1–12}, especially pollution control^{13–19} and surface decontamination^{20,21}. In comparison to traditional thermally activated catalytic processes, NTP technology can provide an alternative way to promote catalytic reactions using highly reactive species such as free radicals, charged ions, atoms, excited molecules and electrons, formed in the plasma discharge by the dissociation of gas molecules in the reaction feed. These processes then initiate the chemical reactions to convert reactants to the desirable products. Importantly, the NTP activates the reactions at relatively low temperatures enhancing their kinetics^{22,23}. Amongst the most commonly studied types of plasma, the dielectric barrier discharge (DBD) offers the advantages of easy implementation of the catalyst within the reactor, stability and convenience for several applications³.

Recently, Stere and co-workers reported the development of a plasma reactor coupled with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for the water gas shift reaction²⁴ and the selective catalytic reduction of NO_x with hydrocarbon (HC-SCR)²⁵. This setup provided insight into the surface processes during the NTP promotion of the catalytic activity. However, the flow configuration within this DRIFTS reactor system was different from

that of a plug flow reactor typically utilised for many such reactions since it consisted of a plasma jet of the gas feed being directed at the surface of the catalyst within the DRIFTS crucible²⁵. In order to simultaneously measure and correlate the spectroscopic and kinetic data under plasma conditions, it is important that the plasma discharge is formed inside the catalyst bed in order to better match the catalytic reaction measurements within a normal plug flow reactor.

The design and application of a fixed bed plasma DRIFTS cell for studying the NTP-assisted heterogeneously catalysed reactions is presently reported. To test and evaluate the performance of this newly-developed plug flow type NTP-DRIFTS system, methane oxidation over Pd/Al₂O₃ catalyst has been investigated. Methane is difficult to oxidise due to its high C-H bond strength and many researchers have investigated methane oxidation under thermal conditions. Relatively high temperatures are usually required to oxidise methane even over Pt and Pd catalysts²⁶ especially in the presence of water. However, it has been reported that Pd-based catalysts are promising for methane oxidation^{25–28}, with their activity being strongly dependent on the nature of the support used (e.g. γ-Al₂O₃, TiO₂, ZrO₂, MgO, MCM-41, Co₂O₃)^{29–33}. Among these catalysts, Pd/Al₂O₃ has been reported to be the most effective candidate for this particular reaction.

Several studies have investigated and attempted to better understand the mechanism of methane oxidation and the nature of the surface species and Pd active sites using *in-situ* DRIFTS, *in-situ* XPS, *in-situ* XRD and DFT calculations^{33–39}. However, the detailed mechanism of this reaction is still under debate. Li *et al.*³⁸ have reported that O₂ can easily adsorb on Pd/Al₂O₃ and Pd/Co₃O₄ to form reactive species, subsequently interacting with CH₄ to form formate (HCOO[–]) and carbonate (CO₃^{2–}) intermediates, which can decompose to CO and CO₂, respectively. Na *et al.*³³ investigated the influence of Zr doping on the Pd/Al₂O₃ catalyst and found that its addition enhanced the number of oxygen vacancies subsequently promoting the activation of gaseous oxygen and the oxidation of

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formate ions to carbonate ions, which in turn improved the oxidation of methane over the Pd/Al₂O₃ catalyst.

Ciuparu and co-authors³⁰ have investigated the surface hydroxyls during methane oxidation over Pd/ γ -Al₂O₃ and reported the direct evidence for their formation and accumulation. They also found that hydroxyl groups derived from the dissociation of water on fully-oxidised PdO produced lower coverage than those derived from the methane dissociation on surface PdO species. They also proposed a dehydroxylation mechanism to form gas phase H₂O.

Schmal *et al.*³⁵ performed *in-situ* XPS and DRIFTS measurements under methane oxidation conditions over different Pd catalysts to study the active sites and adsorbed surface species. They found that the coexistence of PdO/PdO^{δ+} interface enhanced the activity of CH₄ oxidation over the catalyst surface and this was independent of the support used. The DRIFTS analysis for Pd/Al₂O₃ catalyst showed the presence of a PdO/PdO^{δ+} interface after surface activation which allowed the formation of formate and carbonate species.

Additionally, Hellman *et al.*³⁹ investigated the active phase of Pd during methane oxidation using DFT calculations and *in-situ* surface XRD. The DFT calculations over a range of Pd and PdO_x surfaces revealed that either coordinated Pd sites in PdO or Pd metallic surfaces were important for facile dissociation and adsorption of CH₄, which is claimed to be the rate-limiting step for the methane oxidation reaction. Interestingly, and unambiguously, the experimental results obtained by SXRD suggested that high conversion of methane occurred over thick PdO (101) films and metallic Pd, which was consistent with the DFT calculations. The authors pointed out that the established link between high activity and atomic structure enabled rational design of improved catalysts.

In comparison with thermal conditions, non-thermal plasma processes have been shown to be able to overcome the kinetically-restricted methane oxidation reaction at low temperatures^{17,22,40–43}. Although there have been a few *in-situ* studies of plasma catalysis for different reactions^{22,44–46}, there is only one example²² for the NTP-assisted methane oxidation over Pd/Al₂O₃ catalyst. This study probed the role of NTP and the local Pd structure by direct monitoring of the catalyst by X-ray absorption fine structure (XAFS) coupled with end of pipe mass spectrometry. It revealed that the presence of the NTP did not significantly influence the structure of the Pd clusters but resulted in an increase in the temperature of the Pd nanoparticles. However, this differential heating was insufficient to initiate the thermal CH₄ oxidation reaction which suggested that the NTP may play an important role in creating the new reaction pathways and/or assisting similar pathways as those under thermal conditions but with lower activation barriers.

In the present paper, the development of a new plug flow type plasma DRIFTS cell is described in details and applied to the investigation of the surface species present during the NTP-assisted methane oxidation over a Pd/Al₂O₃ catalyst.

2. Experimental

2.1 Catalyst preparation

A 2 wt% Pd/Al₂O₃ catalyst was prepared by incipient wetness impregnation using [Pd(NO₃)₂] (Johnson Matthey, Assay 15.3%) as

the palladium precursor and a SCFa 140 Al₂O₃ (Sasol, BET 140 m² g⁻¹, moisture content 2.72% and pore volume 0.42 cm³ g⁻¹) as the support. The palladium precursor was weighed and dissolved in 12.5 cm³ water which is just under the pore volume for the amount of support used. This aqueous solution was added dropwise to the alumina support under continuous stirring. A small amount of water (less than 1 cm³) was subsequently added via a pipette to the catalyst. The catalyst was dried at 105 °C overnight and calcined in static air at 600 °C for 2 h.

2.2 In-situ DRIFTS-MS Experiments

In-situ DRIFTS measurements were performed using a Bruker Vertex 70 FTIR spectrometer, equipped with a liquid N₂-cooled mercury-cadmium-telluride (MCT) detector. A catalyst sample (50–70 mg) was placed in the ceramic crucible of the *in-situ* DRIFTS cell which outlet was connected to a Hiden Analytical HPR20 mass spectrometer via a heated capillary.

Prior to the *in-situ* DRIFTS measurements, the catalyst was pre-treated to remove any adsorbed water and other adsorbed species by heating in flowing Ar with a total flow rate of 100 cm³ min⁻¹ up to 120 °C for 1 h and then cooled down to room temperature (RT). IR spectra were taken at RT under flowing Ar as background. For the plasma studies, the pre-treated catalyst was exposed to the reaction gas feed at RT for 10 min before switching on the plasma system. The power electrode was driven at ~ 27 kHz with applied peak voltages of 5 or 6 kV. Equations 1 and 2 were used to calculate the plasma power. The discharge electrical parameters were measured using a resistor (10 Ω) for the current and a high-impedance probe (Tektronix, P6015) for the applied voltage, connected to a digital oscilloscope (Tektronix TB51072B).

$$P_{\text{ave}} = \frac{1}{T} \int_0^T I(t)V(t)dt \quad (\text{eq. 1})$$

$$SIE = \frac{P_{\text{ave}}}{\text{Total Flow Rate}} \quad (\text{eq. 2})$$

where P_{ave} is the average power, t is time, T is the cycle period, SIE is the specific input energy, I is the current and V is the voltage.

For comparison with the NTP-activated CH₄ oxidation, the catalyst was tested under thermal activation. Prior to reaction, a pre-treatment under Ar was carried out at 300 °C and data correction included the background subtraction. The thermally activated reaction was carried out between 100 and 400 °C at a rate of 2 °C min⁻¹. For both the plasma and thermal tests, the gases for the reaction mixture were supplied by BOC, *i.e.* 5% CH₄/Ar (99.99%), O₂ (99.99%) and Ar (99.999%) and each gas flow was individually controlled by an Aera^{TM} FC-7700C mass flow controller. The total flow rate of the gas mixture was 100 cm³ min⁻¹. The concentrations of the reactants were 0.5 vol.% CH₄, 10 vol.% O₂, 0.5 vol.% Kr and Ar as balance. End-of-pipe analyses were carried out with a Hiden Analytical HPR20 mass spectrometer (MS). The following mass-to-charge (m/z) ratios were monitored: 15 (CH₄), 16 (O₂, CH₄), 18 (H₂O), 28 (CO), 32 (O₂), 44 (CO₂), and 82 (Kr). Due to the contribution to the MS signal at m/z = 16, of H₂O and O₂, m/z = 15 was used to monitor the CH₄. The contribution of CO₂ at m/z = 28 was accounted for and subtracted during data processing to extract the corrected CO signal.

The IR spectra were recorded with a resolution of 4 cm^{-1} and an accumulation of 128 scans every 60 s. The IR data is reported as $\log 1/R$ ("absorbance")⁴⁷, with $R = I/I_0$, where R is the sample reflectance, I is the intensity measured under reaction conditions, and I_0 is the intensity measured on the sample under a flow of argon. The I_0 background spectrum was recorded at room temperature, immediately prior to the introduction of the reactants mixture.

3. Results and Discussion

3.1 Design of the fixed bed plasma DRIFTS cell

The newly designed plasma DRIFTS reactor aims to replicate as closely as possible the plug flow type reactor with the plasma discharge being generated across the catalyst bed between a central electrode positioned through the centre of the catalyst and a second one on the outside of the reactor.

Figure 1 Schematic sketches of the plug flow plasma DRIFTS cell (a) and base (b).

The DRIFTS cell was composed of two major parts: (1) the base with crucible and (2) the dome with IR windows and cooling system. Figures 1 and 2 show the schematic drawings and photographs of the plug flow plasma DRIFTS cell, respectively.

The catalyst was contained in a ceramic (MACOR®) crucible. A 0.5 mm O.D. heating wire (Kanthal, supplied by Scientific Wire Company) was wrapped around the crucible and had a dual functionality: during the thermal tests or the catalyst pre-treatments it ensured uniform heating of the catalyst; while during the plasma experiments, it was used as an (external) electrode. A K-type thermocouple (TC, supplied by Omega Engineering Limited UK) was placed through the centre of the crucible and was enclosed in a tip-sealed quartz capillary to allow using it as a second (internal) electrode during the plasma tests. Excellent electrical insulation was required for both the heating wire and the thermocouple to prevent arc formation. To further control the discharge area and prevent arc generation, the metallic grid that was previously used to hold the powdered catalyst within the crucible²⁵ was replaced with a quartz wool plug, as shown in Figure 1. To ensure no gas bypass was taking place, the crucible was tightly sealed to the base using two Viton O-rings (Figure 1a). Furthermore, a custom-made (PEEK) union fitting was designed to provide a gas-tight seal for the thermocouple to the base and keep it in place through the centre of the crucible (Figure 1a).

Figure 2 Photographs of DRIFTS cell components (a) and with the plasma on (b).

The DRIFTS base was designed to help with electrical insulation, while maintaining an excellent seal. Two materials have been tested

and used for the manufacturing of the base: polymethyl methacrylate (Perspex) which was used during the setup of the plasma tests since it allowed the user to visualise where the discharge was produced; and polyether ether ketone (PEEK) due to its excellent thermal performance, as well as its chemical and wear resistance properties.

The base contained four channels: two were used for inlet and outlet of the gas feed and two others for water circulation around the dome, to prevent overheating of the ZnSe windows.

A newly developed dome was manufactured entirely from non-conducting materials (Perspex / PEEK) and fitted with ZnSe windows. Water was circulated on the outside of the dome through a Swagelok® perfluoroalkoxy (PFA) tubing to prevent overheating of the windows and formation of toxic hydrogen selenide. Additionally, an identical dome was manufactured of stainless steel for the thermal experiments/treatments. Viton O-rings were used to seal the dome to the base.

The outer dimensions of the new DRIFTS cell (Figures S1 and S2) were designed to ensure its compatibility with the Spectra-Tech™ beam collector. Figures S1 and S2 also provide the detailed dimensions of the custom-made base, ceramic crucible and dome.

3.2 DRIFTS-MS investigation of the CH₄ oxidation

3.2.1 MS analysis

Figure 3 reports the changes in CH₄ conversion as well as CO and CO₂ formation as a function of the switching on and off of the plasma and as a function of the voltage applied over the Pd/Al₂O₃ catalyst and the Al₂O₃ support in the absence of an additional heat source. For both samples, a few general observations can be made:

- when the plasma voltage was increased from 5 to 6 kV, the conversion of CH₄ to CO and CO₂ increased as expected.
- with the NTP on and regardless of the voltage applied, the initial conversion of CH₄ and the initial formation of CO and CO₂ instantly increased, and vice versa with NTP off. However, the profile of the CH₄ conversion, the CO and CO₂ formations were significantly different between the Pd/Al₂O₃ and Al₂O₃ materials.

Figure 3a shows that, at 5 kV, the CH₄ conversion over the Al₂O₃ instantly increased to 18% but then gradually increased to 27% over the course of 27 min reaction time. Similarly, at 6 kV, the evolution of the MS profile showed a sudden increase in conversion of CH₄ as soon as the NTP was switched on but then slowly increased from 33% to 42%. It should be noted that the activity over the Al₂O₃ and blank empty DRIFTS reactor (Figure 3c) was not significantly different, showing a sudden increase followed by a slow but shorter change over ~15 min. This indicates that the gas phase reaction under NTP conditions occurs whether or not Al₂O₃ is present and it could be due to the dead volume of the DRIFTS cell above and underneath the catalyst bed. Thus, while the initial sharp increase in CH₄ conversion is probably due to the gas phase reaction between CH₄ and O₂ in the plasma generated underneath the catalyst bed (Figure 2b), the slow increase in CH₄ conversion may be due surface reactions on the Al₂O₃ support. Figure 3a shows that the difference in CO and CO₂ formation over Al₂O₃ at 5 and 6 kV (corresponding to a SIE of 3.15 kJ L⁻¹ and 4.32 kJ L⁻¹, respectively) was not significant. The ratio of CO₂ to CO, calculated after 25 min

exposure, was 0.95 and 1.22 for 5 and 6 kV, respectively. This trend is similar to that found in the NTP-assisted fixed bed reactor²².

Figure 3 Changes in CH₄ conversion, CO₂ and CO formation as a function of plasma voltage applied to Al₂O₃ (a) 2% Pd/Al₂O₃ (b) and the empty reactor (c) under 0.5% CH₄ + 10% O₂ reaction conditions.

Figure 3b shows that the presence of Pd resulted in a slightly lower conversion at 5 kV compared with the Al₂O₃ and a more steady activity with the conversion reaching 25% compared with 27% for the support alone. A small increase in the CO₂ selectivity was observed for the Pd/Al₂O₃ catalyst compared to the support on

its own. The absence of significant difference, at 5 kV, when comparing to Al_2O_3 , is probably due to the fact that there was insufficient energy available to activate the Pd catalyst. It also indicated that the gas phase reactions were dominant at this voltage (SIE of 2.95 kJ L^{-1}). A substantial change was observed when increasing the voltage to 6 kV. The conversion increased to 60% over 35 minutes on stream, and a similar trend was observed for the production of CO_2 . The fact that this increase in performance was associated with a SIE decrease from 4.32 kJ L^{-1} for the test with Al_2O_3 to 3.5 kJ L^{-1} for the test with the Pd catalyst strongly suggests that the catalytic oxidation of CH_4 over the Pd/ Al_2O_3 catalyst was promoted by the presence of Pd. In contrast, the change in CO formation did not follow the same variation as for the CH_4 conversion and CO_2 formation. Figure 3b shows that the CO formation profile at 6 kV was relatively constant in time while the formation of CO_2 significantly increased in line with the conversion of CH_4 . This suggested that the formation of CO took place via a different reaction pathway than that of CO_2 . This CO formation is likely predominantly taking place through gas phase reaction which is consistent with the somewhat small differences in CO production between the Al_2O_3 and Pd/ Al_2O_3 catalysts at 5 and 6 kV.

To examine the difference between the thermal and NTP activation of the catalyst, the methane oxidation was carried out using a fixed bed quartz reactor as reported elsewhere²². In the case of the thermal activation, Figure S3, it was evident that the catalytic combustion of methane occurred at high temperatures. The methane conversion started at 225°C and reached 100% at $\sim 400^\circ\text{C}$. Al_2O_3 on its own showed very little activity with a conversion lower than 25% even at 400°C . This further confirmed the impact of the NTP on the low temperature methane oxidation.

3.2.2 DRIFTS Analysis

Figure 4 reports the comparison of DRIFT spectra recorded as a function of applied voltage over the Al_2O_3 support and the Pd/ Al_2O_3 catalyst. It should be noted that these spectra were obtained after 20 min under CH_4 reaction conditions; the evolution as a function of time of the surface species at each voltage is included in the ESI (Figures S4-S7).

On applying the voltage to the system, an increase in adsorbed species is observed. It is interesting to note that the timing in changes of the DRIFT spectra was aligned with those of the gas phase CH_4 , CO_2 and CO, detected by mass spectrometer. The DRIFT spectra shown in Figure 4 indicates the presence of gas-phase CH_4 ($\nu_{\text{C-H}}$ at 3016 and $\delta_{\text{C-H}}$ at 1304 cm^{-1})^{34,35,48} and adsorbed H_2O (δ_{OH} at 1640 cm^{-1})³⁴. Both the Al_2O_3 support and the Pd/ Al_2O_3 catalyst showed similar infrared features at 30°C .

At an applied peak voltage of 5 kV, new surface species were formed over the Pd/ Al_2O_3 . The IR band at 1595 cm^{-1} is ascribed to the stretching vibration ν_{OCO} , derived from formate (HCOO^-)^{33,35}. This is also confirmed by the appearance of the IR bands at 1393 and 1376 cm^{-1} , due to the bending vibration ($\delta_{\text{C-H}}$) from formate^{33,35,37}. It should also be noted that, since the conversion of CH_4 at 5 kV is low (see Figure 3), the CH_4 species at 3016 and 1304 cm^{-1} exhibit very little change under NTP and CH_4 reaction conditions.

Figure 4 In-situ DRIFT spectra recorded as a function of plasma voltage applied to Al_2O_3 (grey) and 2% Pd/ Al_2O_3 (black) after 20 min under $0.5\% \text{ CH}_4 + 10\% \text{ O}_2$ reaction conditions at ambient temperature.

At 6 kV, an increase in CH_4 conversion occurred (Figure 3) which also resulted in changes in the surface species over both the Al_2O_3 and the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst (Figure 4). It is noticeable that, especially for the support, additional IR peaks at 2906, 2867, 1700, 1458, 1436 and 1336 cm^{-1} were detected. The IR bands at 2906 and 2867 cm^{-1} are ascribed to the stretching vibration of formate ($\nu_{\text{C-H}}$)^{33,37}. These IR bands coexist with the IR bands at 1393 and 1376 cm^{-1} . In addition, the appearance of IR bands at 1700, 1646, 1436 and 1336 cm^{-1} are due to the formation of carbonate species^{35,49}.

Figure 5 The correlation between CO_2 (MS) and surface formate (DRIFTS) under NTP conditions at 6 kV over $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst.

In order to establish more precisely a relationship between catalytic activity and surface species, a correlation between CO_2 formation and surface formate at 6 kV over Pd catalyst was examined. However, due to the significant contribution of the gas phase reaction between CH_4 and O_2 in the presence of NTP, a good fit was difficult to obtain. The initial increase of CO_2 was predominantly associated with gas phase reaction and the passage through the catalyst bed to the MS, thereafter, the rate of increase in CO_2 formation and the concentration of surface formate were similar which may be associated with the surface reaction under NTP conditions as shown in Figure 5.

It is also noteworthy that, at 6 kV, there are substantial differences between the Al_2O_3 support and the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst with respect to the surface concentration of the adsorbed species. It has been found that surface carbonate and surface formate on Al_2O_3 support were observed, whereas there was little indication of

surface carbonate over the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. In fact, the presence of NTP resulted in the significant formation of surface formate species under CH_4 oxidation conditions over the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. Thus, the role of Pd at 6 kV applied voltage might be to facilitate the activation of oxygen and favour the combustion of all formate species adsorbed on the support, both bidentate (1592 cm^{-1}) and monodentate formates (bands above 1600 cm^{-1}) that form at high coverages^{33,38,50,51}. The increased exotherm would also facilitate CO_2 (derived from carbonate) desorption.

Examining the IR region between 3800 and 3500 cm^{-1} in more detail, there were negative IR bands at 3772 , 3745 , and 3704 cm^{-1} , assigned to hydroxyl groups on the surfaces^{36,37,49}. However, it is interesting to note that significant differences in the hydroxyl groups under reaction conditions, especially for 6 kV, are observed between Al_2O_3 and $\text{Pd}/\text{Al}_2\text{O}_3$. Figure 4 also shows that the Al_2O_3 support showed stronger negative IR bands between 3775 and 3700 cm^{-1} than the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, suggesting that there was a more substantial consumption of these hydroxyl species on the Al_2O_3 . Föttinger *et al.*⁵⁰ investigated the mechanism of carbonate formation over a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst and confirmed that the interaction between CO and hydroxyl groups on the Al_2O_3 support resulted in the production of HCOO^- species, which subsequently interacted with O_2 to form carbonate species.

As noted earlier, the surface species adsorbed on the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst under NTP and CH_4 oxidation conditions mainly corresponded to formate species with a very small amount of adsorbed carbonate. Given that, at 6 kV, the transient profiles of both CH_4 conversion and CO_2 formation were similar upon turning the plasma on, but were different from that of CO formation, this would indicate that the formation of CO_2 goes via a different route from that of CO formation. A similar behaviour is observed for the thermal case by Li *et al.*³⁸, who investigated the mechanism of CH_4 oxidation reaction over a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst by performing *in-situ* IR measurements under reaction conditions. It was reported that both HCOO^- and CO_3^{2-} intermediates were formed during the reaction, which subsequently decomposed to form CO and CO_2 , respectively³⁸. The quasi absence of carbonate on the surface of the palladium catalyst under NTP exposure would indicate that their decomposition was promoted under these conditions. The surface formate may be associated with the reaction of CO interacting with surface hydroxyl groups as reported by Föttinger *et al.*⁵⁰.

Figure 6 Comparison of *in-situ* DRIFT spectra recorded over 2% Pd/Al₂O₃ as a function of reaction temperature and plasma at ambient temperature at 6 kV under 0.5% CH₄ + 10% O₂ reaction conditions.

Figure 7 Schematic diagram representing the reaction mechanism of CH₄ oxidation the possible pathways of CO₂ formation under thermal and plasma conditions.

To better understand the differences between NTP and thermal catalytic activation, *in-situ* DRIFTS measurement using a high temperature DRIFTS cell was carried out over the Pd/Al₂O₃ catalyst. Figure 6 reports the comparison of the spectra recorded as a function of reaction temperature under thermal conditions with those recorded under NTP conditions at 6 kV. The DRIFTS results revealed that the distributions of surface species over the Pd/Al₂O₃ catalyst under thermal conditions from 100 to 400 °C were significantly different to that obtained during the NTP-activated experiments. Figure 6 shows that the formation of surface formate (2906, 1592, 1393, and 1373 cm⁻¹)^{33,35,37} is predominant under NTP conditions while the majority of surface species under thermal conditions are carbonate (1541, and 1341 cm⁻¹)^{35,50}. This suggests that the reaction pathways for NTP and thermal conditions may be different, with the oxidation of CH₄ to CO₂ probably going via formate and carbonate routes, respectively.

The results obtained with the NTP activated CH₄ oxidation can be rationalized (as shown in Figure 7) using the reaction mechanism reported in the literatures for high temperature thermal activation^{31,33,35,36,38}. Following the methane and oxygen adsorption, methyl and OH groups are formed. Further reaction leads to the formation of CH_x and C species, which can interact with adsorbed O to give CO, CO₂ and carbonate. Additionally, both gas phase and surface CO can interact with OH groups to form formate, which are subsequently decomposed to give CO₂. According to our results, it is possible that the reaction takes mainly place via the carbonate route in the thermal case, while the oxidation occurs via the formate route under plasma conditions.

4. Conclusions

The new design of a plug flow type plasma DRIFTS reactor has been reported and evaluated through a model reaction i.e. the oxidation of methane over a Pd/Al₂O₃ catalyst. Using the plasma DRIFTS cell coupled with mass spectrometry has allowed showing that NTP significantly enhances the formation of surface species, i.e. formate and carbonate, under methane oxidation conditions. Comparative analysis of the spectroscopic results with those obtained under thermal activation indicate that the reaction pathways for NTP and thermal conditions may be different.

Conflicts of interest

There are no conflicts to declare.

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