Probing the role of a non-thermal plasma (NTP) in the hybrid NTP-catalytic oxidation of CH4

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**Abstract:** Three recurring hypothesis are often used to explain the effect of non-thermal plasma (NTP) on NTP-catalytic hybrid reactions, namely, modification or heating of the catalyst or the ability of plasma produced species to open up new reaction pathways. By directly monitoring the catalyst by X-ray absorption fine structure (XAFS) coupled with end of pipe mass spectrometry the NTP assisted CH4 oxidation over Pd/Al2O3 was investigated. This *in situ* study has shown that the catalyst did not undergo any significant structural changes under NTP conditions. However, the NTP did lead to the Pd nanoparticle temperature increasing but this temperature rise was insufficient to activate the thermal CH4 oxidation reaction. The contribution of a lower activation barrier alternative reaction pathway involving the formation of CH3(g) via electron impact reactions is proposed.

Methane is a major contributor to climate change, with a global warming potential at least 21 times higher than that of CO2, consequently, its release into the atmosphere must be stringently controlled. In addition to controlling the release from landfill, biomass burning and from leakage from natural gas storage and distribution, emission abatement due to methane slip in automotive vehicles must also be addressed.

One solution is to use catalytic total oxidation to produce CO2 and water. Palladium is a known efficient catalyst for methane oxidation, and has been studied extensively with varying hypotheses of the active phase being reported, from a PdO-like phase to Pd0.[1] Unfortunately, of all the catalysts currently reported, none are sufficiently active under cold start conditions, with most catalysts requiring light-off temperatures of around 400°C.[2] Such high temperatures are required due to the high activation barriers for the dehydrogenation of CH4 to form surface adsorbed CH3\* and H\* which is thought to be the rate determining step. For example, Jørgensen *et al.* predicted that the extraction of the first H from CH4, had an activation barriers of 0.99 and 0.79 eV over Pd(111) and Pd(100), respectively.[3] One known method of inducing catalytic activity for kinetically restricted reactions at low temperatures is the coupling of non-thermal plasmas (NTPs) with catalysis. Recent examples are the selective catalytic reduction of NOx, VOC removal and water gas shift without the need of an external heating source. Similarly, the NTP assisted CH4 oxidation has been reported at both low temperature, where no additional heat source is applied, and at elevated temperatures, where the catalyst is also heated to temperatures up to 300 °C.[4]

Three recurring hypotheses are often proposed to explain the assistance which NTP’s give to catalytic reactions. Firstly, that the plasma modifies the catalyst, secondly, that the plasma heats the catalyst, and thirdly, that the assistance of the plasma permits new reaction pathways to occur. The NTP has been shown, in some cases, to alter the catalysts itself by, changing the oxidation state[5] or metal surface area [6,7] of the components. Several attempts have been made to determine the temperature of a catalyst during NTP reactions, using thermocouples placed near or in the catalyst bed, via infrared cameras or optical emission spectroscopy.[8] However, no study has yet directly measured the temperature of the metal nanoparticles within the catalyst and compared this with the overall bed temperature during a NTP assisted catalytic reaction. The interaction of radicals, electrons or photons produced by the NTP with the catalyst and the adsorbed molecules may open up new reaction pathways, for instance the direct reaction of gas phase radicals with adsorbed species, i.e. a direct Eley-Rideal mechanism could occur.[9] Desorption from the catalyst surface may also be aided by electron impact.[10] To investigate which of these hypotheses are operating under NTP assisted catalysis, *in situ* investigations are crucial. Whilst very few *in situ* combined plasma catalysis studies have been performed,[11] one recent example is the investigation of the hydrocarbon selective catalytic reduction (HC-SCR) of NOx over Ag/Al2O3.[12] This investigation used a modified DRIFTS set up to follow the adsorbates during the thermal and the NTP enhanced reactions; providing invaluable information on adsorbed species and the mechanism of the reaction. However, to the best of our knowledge, no *in situ* structural studies have been undertaken to characterize the catalyst during NTP assisted reactions. In the study reported herein, we have probed the NTP assisted CH4 oxidation, in the absence of any applied external heating, using *in situ* XAFS spectroscopy. The results provided significant new insights into the role of plasma induced heating effects in the NTP assisted process.

The NTP activated oxidation of CH4 over a 2% Pd/Al2O3 (sample 1, Table S1) was examined at applied voltages of 6 and 7 kV at 22.5 kHz. In the absence of an externally applied heating source, 55% (6 kV) and 67% (7 kV) CH4 conversions were observed. In the presence of the catalyst high selectivities were found (CO:CO2, 1:10.8 (6 kV) and 1:11.5 (7 kV)) and negligible amounts of H2 were formed. In addition, a temperature programmed oxidation measurement of the catalyst following the methane oxidation showed that little carbon oxidation (>600 oC) had occurred (Figure S1). It should be noted that, in the absence of the catalyst, although the conversion was similar (68% at 7 kV), significantly more CO was formed (CO:CO2, 1:1.1). This may also be compared with the reaction over the support alone in the presence of the plasma which had a reduced conversion of 59% and a CO:CO2 ratio of 1:2.1. These demonstrate the importance of the catalyst on determining the selectivity of the reaction. The specific energy input (SEI) calculated for the 6 and 7 kV plasma in the presence of the catalyst was 2.133 kJ L-1and 2.637 kJ L-1, respectively.

Similar conversions/selectivities were also obtained during the XAFS spectroscopy investigation monitored by end of pipe mass spectrometry analysis (sample 1, 52% conversion at 6 kV, Figure S2). The setup, shown in Figures 1 and S3, allowed XAFS measurements along the length of the packed catalyst bed to be monitored. XAFS measurements were performed at the Pd K-edge on the B18 beamline at the Diamond Light Source, UK.

**Figure 1.** Setup for *in situ* measurements using XAFS spectroscopy coupled with MS for methane oxidation using plasma.

The X-ray absorption near edge structure (XANES) spectra of the fresh catalyst (sample 1), under thermal CH4 oxidation reaction (352 °C) and under CH4 oxidation using the plasma are very similar as shown in Figure 2. On first inspection, there is little impact of the plasma on the catalyst, with the spectra closely resembling that of PdO. When oxygen is removed from the system under plasma, leaving just 5000 ppm CH4 and He balance, the catalyst is reduced, as shown by a shift in the edge position of 2 eV and the spectra are very similar to that of the Pd foil reference. Analysis of the extended X-ray absorption fine structure (EXAFS) region, reveals only very subtle differences in the spectra when comparing the plasma activated case and in the absence of plasma, under CH4 oxidation conditions. Spectra collected at two positions, 2.5 mm and 7.5 mm from the start of the catalyst bed are shown in Figure 3 and the fitting parameters are shown in Table 1. In both cases the oscillations are dampened when the plasma is on compared to when it is off. No other differences are observed in the spectra, for example no shift in phase or additional features are observed which would indicate changes in distance to nearest neighbours or changes in the co-ordination around the absorber atom. Furthermore, on turning off the plasma, no change was found compared with the fresh catalyst (Figure S4) demonstrating the reversibility of the changes and indicating that no significant permanent changes to the nanoparticle structure had occurred. It should be noted that XAFS is a bulk averaging technique, therefore, we cannot exclude that some minor non-reversible changes to the Pd nanoparticles may occur, which are below the detection level of the technique. However, the EXAFS results are consistent with transmission electron micrographs of the catalyst before and after the plasma treatment which showed similar particle sizes 2.1 ± 1.0 and 2.9 ± 1.4 nm and no change in the shape of the nanoparticles observed (Figure S5).



**Figure 2.** Normalised XANES spectra of the Pd foil reference, PdO reference, the fresh catalyst (sample 1) under helium, the catalyst during the thermal CH4 oxidation reaction, during the plasma activated CH4 oxidation and during CH4 only reaction under plasma conditions.

**Figure 3.** k2χ(k) data of CH4 oxidation at the start (position 2.5) and middle (position 7.5) of the catalyst (sample 1) bed, under plasma on and plasma off conditions and the CH4 only experiment under plasma on and off conditions.

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| **Table 1.** EXAFS Fitting Parameters for Pd K-Edge spectra taken under CH4 oxidation and CH4 only conditions for sample 1. | | | | | | | |
| Conditions | Absorber-Scatterer | E0 (eV) | CN[c] | Reff (Å) | 2 | 2  (plasma on data) | Temperature (plasma on (°C)) |
| [a]CH4 oxidation, plasma off, front 2.5 mm) | Pd\_O | -0.7(8) | 4.2(6) | 2.024(6) | 0.0025(6) | 0.0043(5) | 203±32 |
| Pd\_Pd1 | 4.2(6) | 3.058(6) | 0.0059(8) | 0.0099(7) |
| Pd\_Pd2 | 4.9(8) | 3.445(6) | 0.0054(9) | 0.0095(9) |
| [a]CH4 oxidation, plasma off, middle (7.5 mm) | Pd\_O | 3.9(2) | 3.9(2) | 2.026(5) | 0.0022(5) | 0.0038(4) | 152±28 |
| Pd\_Pd1 | 4.3(6) | 3.059(6) | 0.0059(7) | 0.0088(6) |
| Pd\_Pd2 | 4.7(8) | 3.449(6) | 0.0053(8) | 0.0092(8) |
| [b]CH4 cracking, plasma off, middle (7.5 mm) | Pd\_Pd1 | 5(1) | 7.5(5) | 2.76(9) | 0.0057(2) | 0.0097(7) | 207±32 |
| Pd\_Pd2 | 2(2) | 3.8(6) | 0.0081(1) | 0.0158(9) |
| [a] Fitting parameters: S02 = 0.85 as determined by the use of a Pd foil standard; Fit range 3.0 < k < 16.0, 1. < R < 3.5; number of independent points = 20.5.  [b] Fitting parameters: 1.2 < R <4, 3.4 < k < 10.6, number of independent points = 12.6 | | | | | | | |

We propose that this subtle dampening of the oscillations is due to an increase in the temperature of the palladium under the application of the plasma, with the mean squared thermal disorder parameter (σ2) increasing and consequent decreasing the amplitude of the EXAFS oscillations. Similarly weak oscillations were also observed for a range of catalyst loadings and particle sizes (samples 1-4, Table S1) under plasma conditions. As no other measurable changes occur to the catalyst, the change in σ2 can be used to estimate the temperature of the Pd nanoparticles on the catalyst. A data set was obtained on cooling the catalyst from 500 °C to room temperature under air. This showed no structural changes on cooling and was used to determine a calibration curve of the variation of σ2 with temperature.

The calibration curve and fitting parameters are shown in the supplementary information, Figures S6-S9 and Tables S2 and S3. This data was then used to determine the temperature of the catalysts when activated by the plasma. To fit the data upon cooling, the EXAFS fit was performed allowing the coordination numbers (CN), σ2 values and distances to refine. The determined CN’s were then fixed when fitting the plasma activated spectrum, allowing only σ2 and distances to refine. This value was then used to estimate the temperature of the catalyst when activated by the plasma (Table S4). For all the catalysts studied the estimated temperatures ranged from 138 to 179 oC in the middle of the bed. In addition, measurements were made for sample 1 comparing the front and middle of the bed and the temperatures were determined as 203 ± 32°C and 152 ± 28 °C, respectively. The fitting data (Table 1) and the data and fit are shown in Figure S7. The higher temperature at the front of the bed is expected as the CH4 oxidation is exothermic and the rate will be highest towards the start of the bed of catalyst. Using Aspen software (Aspen Technology), a simulation of the reaction using the same reactants concentrations and assuming thermodynamic equilibrium (i.e. full methane conversion) provided a reactor temperature of ~210 °C; which is consistent with the exothermicity of the CH4 oxidation.

These estimated temperatures of the catalyst bed are significantly higher than those measured using an IR camera, Figure 4 (60-90 oC), which is a technique commonly used to determine plasma reaction temperatures. [8] This is not surprising as the IR camera predominantly measures the outside wall of the reactor and will significantly underestimate the temperature within the packed bed.

**Figure 4.** Temperature profile along the catalyst bed (x direction) using an infrared camera, where x are arbitrary units, dependant on the camera focus.

To determine if the observed heating of the catalyst was due to the exothermicity of the CH4 oxidation reaction or induced by the plasma, the reaction was performed in the absence of O2. Under these conditions the reaction of methane is endothermic and results in coupling products.[13] During the endothermic non-oxidative CH4 coupling, the EXAFS data, shown in Figure 2, when the plasma is both on and off resembles that of the Pd foil, therefore, the PdO catalyst has been, unsurprisingly, reduced on removal of oxygen from the feed gas. Using the value of σ2 calculated from this data, the estimated temperature during the plasma was 207 ± 32 °C (Table 1). From these results we conclude that the plasma is responsible for the observed heating effect.

The fact that there is no significant nanoparticle size or catalyst loading dependent changes on the temperatures calculated from the XAFS may suggest that the surface of the whole catalyst (nanoparticle and oxide) is being heated. The XAFS data only probes the Pd and this, however, does not preclude the alumina surface from also being heated. In this case the support and nanoparticle would be in thermal equilibrium, therefore, leading to similar changes in temperature for all the catalysts studied.

Taking account of all the data acquired, the estimated temperature of the nanoparticles during NTP activated CH4 oxidation is 162 ± 24 °C, within the error of the calculated temperature from the exothermicity of the methane oxidation reaction. Therefore, a clear difference in temperature is observed between the EXAFS estimation and that measured via the infrared camera. Almost a two-fold increase in temperature of the nanoparticles is measured compared to the overall temperature of the catalyst bed. However, this temperature (162 °C) is not high enough to activate the thermal reaction, as observed from the light-off curve of the thermal reaction for sample 1, shown in Figure 5.



**Figure 5.** Light-off profile 5000 ppm CH4, 5% O2, 5% Ar and He balance.

This *in situ* study has provided evidence to address the hypothesis proposed regarding the role of the NTP in the hybrid catalytic reaction. Herein, it is clear that no significant structural changes are found within the catalyst on application of the NTP under CH4 and CH4+O2 conditions. In addition, the NTP heats the Pd nanoparticles but the temperature of the nanoparticles is lower than that necessary to activate the thermal CH4 oxidation reaction. It is, therefore, likely that an alternative methane activation pathway is in operation, having a lower activation barrier than the thermal activation reaction. As noted the rate limiting step for the thermal reaction over Pd is the formation of the CH3(a) + H(a). This is found above 227 oC whereas carbon oxidation is rate limiting below 227 oC.[3] Interestingly, the major effect of the plasma on methane has recently been reported to be the formation of CH3(g) via electron impact reactions.[14] Given the fact the nanoparticle temperatures are approximately at the transition point where methane activation becomes rate limiting, it is likely that the plasma activation of methane in the gas phase then leads to a reduced activation barrier for the surface process and thus the ability of the NTP-process to occur at much reduced temperatures. It cannot be discounted that the Pd nanoparticles may become more defective in the presence of the plasma and more open faces have been reported to offer a lower activation barrier for CH4 dehydrogenation.[3] However, this effect is likely to be small compared with the pre-activation of the CH4 in the gas phase under plasma conditions.

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**Keywords:** non-thermal plasma • EXAFS spectroscopy • oxidation• heterogeneous catalysis • methane

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**Entry for the Table of Contents**

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| COMMUNICATION | | |
| Text for Table of Contents  CH4 combustion has been undertaken using a hybrid non-thermal plasma-Pd based catalyst system without heating the catalyst bed. Using *in-situ* X-ray absorption spectroscopy no significant structural changes were found in the catalyst. Although, the plasma was found to heat the Pd nanoparticles, this was not sufficient energy to activate the reaction leading to a proposed alternative reaction pathway. |  | Author(s), Corresponding Author(s)\*  Emma K Gibson,\* Cristina E Stere, Bronagh Curran-McAteer, Wilm Jones, Giannantonio Cibin, Diego Gianolio, Alexandre Goguet,\* Peter P. Wells, C. Richard A. Catlow, Paul Collier, Peter Hinde, Christopher Hardacre\*  Title  Probing the role of a non-thermal plasma (NTP) in the hybrid NTP-catalytic oxidation of CH4 |
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