Mechanistic Aspects of Plasma-Enhanced Catalytic CH₄ Decomposition: Surface Infrared Measurements of CH_x Oxidation and CO formation on Ni Catalyst

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Abstract: Real-time diffuse reflectance infrared Fourier transform spectroscopy results are reported for partial CH₄ oxidation using a Ni catalyst in combination with an atmospheric pressure plasma jet (APPJ). Formation/removal of CH_x and CO on the Ni surface are seen during plasma-enhanced catalytic oxidation of CH₄ as APPJ-catalyst separation and catalyst temperature are varied, and shed insight on respective roles of plasma particle fluxes and catalyst temperature on surface processes during CH₄ partial oxidation.

Keywords: Atmospheric pressure plasma, catalysis, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), partial methane oxidation, catalyst surface modification.

1.Introduction

Cold atmospheric pressure plasma (CAP) assisted thermal catalysis has shown promise to enhance catalytic efficiency by a process called plasma-catalyst synergy (PCS) [1]. The overall goal of this work is to obtain mechanistic insights on surface phenomena in PCS. The system chosen is cold plasma assisted partial oxidation of methane using a Ni catalyst. The evaluation of gas phase and surface changes as a function of feed gas composition, catalyst temperature and time provides information on plasma-catalyst interactions during chemical conversion. In a prior publication [2] results of remote gas phase characterization by IR absorption spectroscopy has been reported for this system, and a synergistic effect of plasma assisted catalysis was seen for gas phase CO production. Moreover, it was found that at higher catalyst temperature of ~ 500 °C the formation of gas phase CO was reduced. In the present work we report initial results of surface changes of a Ni catalyst as it assists partial oxidation of methane in the presence of cold plasma produced particle fluxes.

2. Experimental setup

For CAP-assisted partial oxidation of methane by a Ni catalyst we employ a flexible Ar atmospheric pressure plasma jet (APPJ). The APPJ is composed of a RF driven tungsten needle, a grounded copper ring and a quartz dielectric tube in between them. The RF frequency of the APPJ is around 13.56 MHz. Additional details on the APPJ can be found in [3].

The plasma jet itself is fed by 200 sccm Ar, to which up to 0.5% of oxygen is added to enhance the chemical reactivity. Separately, 2 sccm $CH_4/400$ sccm Ar is admitted through the inlet of the reaction chamber. The setup is shown in figure 1.

The plasma jet is integrated into a reaction chamber via one of the ports, the other two of which are sealed by KBr lenses. The IR light goes through the interaction zone of the plasma jet and supported Ni powder catalyst and is guided by the two KBr lenses. The silica/alumina supported Ni catalyst (Alfa Aesar 31276) in powder form is placed inside the holder and forms a stable catalyst surface on top. A heater is used for varying the catalyst temperature from room temperature up to 500 °C. In infrared diffuse reflectance Fourier transform spectroscopy (DRIFTS) the incident IR light is diffusely reflected by the rough catalyst surface formed by Ni catalyst powder (~40 um) and collected for detection. The present setup is similar to that used by Stere et al. [4]. For a more complete description of the experimental setup and DRIFTS technique, the reader is referred to Knoll et al.[2].



Fig.1. Schematic of DRIFTS setup used for studies of plasma assisted catalysis. Ar or Ar/O_2 flows through the APPJ, whereas Ar/CH_4 is fed into the reaction chamber without passing through the APPJ.

3. Results and discussions

We first present an overview of the plasma effect on the Ni catalyst at two different plasma plume-catalyst surface distances (3 mm and 8 mm). These experiment were

performed over very long times, and in figure 2, selected traces of the long-time experiments at a catalyst temperature of 25 °C are shown. Ar plasma is excited using 200 sccm Ar flow through the plasma jet tube. Separately, 2 sccm CH₄ in 400 sccm carrier Ar gas is injected into the chamber. The total Ar flow and methane are supplied continuously from the beginning. Trace #31 at 3 mm (corresponding to a total experimental time of 13.95 min since measurement of each FTIR trace took 25 s) and #71 at 8 mm distance (31.95 min) were obtained without plasma excitation and using 2 sccm CH₄ and a total of 600 sccm Ar flow. Several FTIR peaks are seen, including CH₄ and CO₂. A more detailed examination of these spectra shows the formation of FTIR peaks near ~2930 cm⁻¹ and 2864 cm⁻¹ at both distances as a result of supplying 2 sccm CH₄ to the reactor and before striking a plasma. This indicates that at room temperature, methane is adsorbed on the powder catalyst surface, leading to formation of the observed CH_x spectral features. In addition, the CH₄ FTIR peak is observed at 3016 cm⁻¹. This peak is most likely due to IR absorbance by gas phase methane inside the dome reactor, since the CH₄ FTIR peak vanishes immediately when the CH₄ gas supply is shut off.

Subsequently, the Ar discharge is established with a dissipated power of 2 W. Traces #122 (3 mm) and #235 (8 mm) correspond to this. The figure shows that at both plasma-source-catalyst distances of 3 and 8 mm O-H stretching (~3450 cm⁻¹) and O-H bending (1620 cm⁻) modes are observed. CH_x and CO related peaks between 3000 cm⁻¹ and 2000 cm⁻¹ showed significant differences for 3 and 8 mm treatment distances, and details will be shown below. The peak near ~ 1573 cm⁻¹ is potentially related to C=C. The feature at ~1280 cm⁻¹ is quite close to the C-O bond in the form of carboxylic acids. The broad peak near ~1000 cm⁻¹ is tentatively assigned to Si-O-C.

A more detailed investigation of the spectra shows in this case that at 3 mm plasma-source catalyst distance, the 2930 cm⁻¹ and 2864 cm⁻¹ spectral features vanish once the plasma is established. As the plasma exposure of the catalyst is increased, a new peak forms at ~ 2840 cm⁻¹ and can be related to CH₂ [5],[6]. This peak gradually increases as the plasma jet contacts the Ni catalyst for an extended time. For a plasma plume-catalyst surface distance of 8 mm, the ~2930 cm⁻¹ and 2864 cm⁻¹ FTIR features also disappear when the plasma is switched on. In this case the formation of three C-H_x features, i.e. ~2976 cm⁻¹, ~2940 cm⁻¹ and ~ 2880 cm⁻¹ are seen, which can be attributed to CH₃, CH₂, and CH respectively [5],[6].



Fig. 2. Comparison of DRIFTS spectra at plasma plumecatalyst surface distances of 3 and 8 mm. The numbers at the left correspond to the scan number (each scan took 25 s). For a detailed explanation see text.

Traces #170 and # 365 correspond to an experimental situation when subsequently both the plasma and CH_4 supply have been switched off. The formation of CH_x surface species on the Ni catalyst which persist after both the plasma and CH_4 gas supply are shut off is seen in Fig. 2. The FTIR traces #170 at 3 mm and #365 at 8 mm, respectively show that the CH_x peak formed during the plasma treatment persevere. Additionally, for 8 mm source-catalyst separation significantly more CH_x is seen than for 3 mm separation.

3.1 The effect of Ar and Ar/O₂ discharge on CO bond formation

The presence of CO and CO₂ related features is of special interest. One important observation is that at both 3 and 8 mm plasma source-catalyst separation, CO species are formed on the catalyst surface once a pure Ar discharge is ignited. The observation of CO is highly characteristic of the plasma excitation. Since no O₂ was added in this case, the source of oxygen is either from residual CO_2 or O_2 impurities in the setup along with potentially oxygen from the oxidized Ni surface. The CO related spectral features persist after both the plasma and CH₄ gas supply are shut off – see scans # 170 at 3mm and # 365 at 8mm in Fig. 2, respectively. This observation is consistent with these being surface-related features. Figure 2 also shows that at 3 mm plasma source-catalyst separation distance the CO signal is much larger than at 8 mm, consistent with the key role of plasma in the formation of CO.

In order to study the temperature effect on CO bond formed on catalyst surface, a series of experiments was performed using pure Ar discharges and Ar/O_2 discharges.



Fig. 3. CO evolution under Ar plasma. The reaction conditions are the same as used for Fig. 2. 200 sccm Ar (through the discharge tube) and 2 sccm CH_4 in 400 sccm Ar (downstream) are fed continuously to the apparatus from the beginning (-5 min). The pure Ar plasma is switched on at 0 min. The time is shifted so the ignition of plasma coincides with 0 min. For 25 °C at 3 mm case, pure Ar plasma is switched off between 5 and 11 min to determine the dependence of C-O bond on plasma itself.



Fig. 4. CO evolution under the influence of Ar/O_2 plasma. The Ar/O_2 discharge is excited using RF with 200 sccm Ar plus 1 sccm O_2 flowing through the discharge tube. 2 sccm CH_4 in 400 sccm Ar is fed continuously downstream from the source to the catalyst.

Figure 3 shows the CO bond formation as a result of an Ar discharge. In this case no O_2 is added, so any oxygen is added inadvertently, e.g. by gas impurities like background CO_2 . Oxidation of the CO is weak in this

case, and as a result the effect of catalyst temperature and plasma source-catalyst separation distance on the CO peak intensity can be studied. The CO FTIR peak is connected with the catalyst surface since it persists after the reactive gases have been removed (see Fig. 2). Figure 3 shows that when the plasma source-catalyst separation distance is 3 mm, the CO-related FTIR intensity is increased relative to that seen for treatments at a treatment distance of 8 mm. This clearly shows that intensifying the plasma treatment increases CO formation.

When the catalyst temperature is increased to 500 °C, the formation of CO is stronger than with the catalyst temperature at a temperature of 25 °C. Figure 3 also shows that there is little CO formation when the catalyst is heated to 500°C without plasma. Overall, Fig. 3 shows a strong plasma-catalyst synergy effect for CO formation since low catalyst temperature and for large catalyst-source separation, CO formation on the catalyst surface is much weaker.

When oxygen is added to the discharge, CO on the catalyst surface strongly oxidizes by the ROS produced by the Ar/O_2 discharge. This is shown by Fig. 4. For an ROS abundant environment, oxidation determines the CO bond evolution.

At 3 mm, ROS produced by the plasma can enhance CO formation on the catalyst briefly after the Ar/O_2 discharge has been switched on. This effect is much stronger at a catalyst temperature of 25°C than at 500°C. At both temperatures a maximum is reached and subsequently the surface CO signal is reduced. This shows that the loss of CO by oxidation is promoted by increasing the catalyst temperature and the intensity of the oxidizing species flux from the APPJ. Figure 4 shows that at plasma source catalyst distance of 3 mm with the catalyst temperature at 500 °C, the CO related signal has almost vanished after 10 min of plasma operation. Without plasma excitation the CO related signal is always insignificant (results are only shown for 500°C in Fig. 4).

The long-time oxidation of CO and reduction of the CO DIFTS signal is also seen for the 8 mm plasma sourcecatalyst separation distance. A strongly accelerated CO peak evolution is seen at the higher substrate temperature.

Corresponding results have also been obtained for CH_x and other moieties on the catalyst surface, but cannot be reported because of space limitations. These will be described in a more comprehensive article in the future.

4 Conclusions.

A real-time, in-situ study of plasma-assisted partial oxidation of methane by a Ni catalyst shows that for larger plasma source-catalyst separation and pure Ar operation more CH_x and less CO surface related FTIR absorption is seen than for closer plasma source-catalyst

distance. As the plasma jet is moved closer to the catalyst surface and the role of plasma-related species fluxes is increased, the intensity of the CH_x species on the surface is reduced, while the intensity of CO FTIR absorption increases. When the plasma jet is moved closer to the catalyst, reactive species like O oxidize CH_x species on the surface, and increase the intensity of CO (e.g. as seen from the behavior of the ~ 1280 cm⁻¹ feature in figure 2). These processes are accelerated when the Ni catalyst temperature is increased to 500°C. For Ar/O₂ operation of the APPJ the work shows that more intense plasma interaction with the catalyst (smaller plasma source-catalyst separation) and elevated catalyst temperature accelerate the more complete oxidation of surface bound CO.

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References

- [1] J. C. Whitehead, "Plasma–catalysis: the known knowns, the known unknowns and the unknown unknowns," *J. Phys. D: Appl. Phys.*, vol. 49, p. 243001, Jun 2016.
- [2] A. J. Knoll, S. Zhang, M. Lai, P. Luan, and G. S. Oehrlein, "Infrared studies of gas phase and surface processes of the enhancement of catalytic methane decomposition by low temperature plasma " *J. Phys. D: Applied Physics*, vol. xxx, p. xxx, 2019.
- [3] S. Q. Zhang, W. van Gaens, B. van Gessel, S. Hofmann, E. van Veldhuizen, A. Bogaerts, *et al.*, "Spatially resolved ozone densities and gas temperatures in a time modulated RF driven atmospheric pressure plasma jet: an analysis of the production and destruction mechanisms," *Journal of Physics D-Applied Physics*, vol. 46, p. 205202, May 2013.
- [4] C. E. Stere, W. Adress, R. Burch, S. Chansai, A. Goguet, W. G. Graham, *et al.*, "Probing a Non-Thermal Plasma Activated Heterogeneously Catalyzed Reaction Using in Situ DRIFTS-MS," *Acs Catalysis*, vol. 5, pp. 956-964, Feb 2015.
- [5] L. J. Bellamy, "Amides, proteins and polypeptides," in *The infra-red spectra of complex molecules*, ed: Springer, 1975, pp. 231-262.
- [6] B. Suart, "Infrared Spectroscopy: Fundamental and Applications," ed: John Wiley & Sons, Ltd, 2004.