Non-Thermal Plasma Conversion of N2, CO2 And CH4

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Abstract. This paper reports in-situ Fourier Transform Infra Red (FTIR) spectroscopy was employed to study the plasma glow region of a non-thermal plasma (NTP) using Macor®, SnO2 – coated Macor® and CeO2 – coated Macor® as dielectrics and fed with CO2, CH4 and N2. This chemical system was chosen as a model to explore the application of in-situ FTIR spectroscopy to the study of NTP chemistry during plasma processing and the data obtained were compared to those using uncoated Macor®. Initial experiments investigated the possible reaction of CO2 and N2 in plasma system followed by studies using CH4, CO2 and N2 as the feed gas. Macor®, a ceramic consisting of the oxides of Al, Mg, and Si was chosen to provide benchmark data as it was not expected to be catalytic active and had a reasonable constant (ca 6 over the range 1 kHz - 6 GHz) and thermally stable. The study of the non-thermal plasma process at uncoated Macor® led to unexpected chemistry whilst replacing it with SnO2 – coated Macor® were somewhat different with no reaction taking place in plasma-driven experiments on SnO2.

1. Introduction

Non-thermal plasmas (NTPs) are a gaseous mixture of high energy electrons, ions and radicals and are generated not by high temperatures but by electric fields typically at room temperature and pressure. Even at ambient temperature the electrons can be at temperatures of 1000s of K, allowing reactions to take place that would not usually be observed until hundreds or even thousands of K above ambient [1-4]. This is the advantage of non-thermal plasma process where it can produce species, active and intermediates products viable without requiring extreme temperature [4].

Generally, NTPs can promote chemical reactions of reactants and by adding a catalyst, the chemical processes in a plasma can be speed up [3]. There are numbers of studies on non-thermal plasma catalysis, such as work of Wang et al. [5] who studied CO2 and CH4 conversion using three different catalyst materials in a dielectric barrier discharge (DBD) reactor. His work showed that non-
thermal plasma catalysis improved the chemical conversion of CO$_2$ and CH$_4$ and the selectivity of gaseous products compared to the analogous thermal process, see Figure 1.

Figure 1. A comparison of CO$_2$ and CH$_4$ conversion and gaseous products selectivities for catalysis activation only, plasma-induced conversion and plasma catalysis for three different catalyst materials in a DBD reactor at 30 °C and atmospheric pressure. Adapted from Wang et. al. [5], Bogaerts and Neyts [6] and Ali [7].

Figure 2. A comparison of CO$_2$ and CH$_4$ conversion and liquid products selectivities for catalysis activation only, plasma-induced conversion and plasma catalysis for three different catalyst materials
in DBD at 30 °C and atmospheric pressure. Adapted from Wang et al. [5], Bogaerts and Neyts [6] and Ali [7].

As can be seen from Figure 1, H₂, CO and C₂H₆ gaseous were found to be the major products in the plasma and plasma catalysis experiments and interestingly, the selectivities of the liquid products were different when Pt/Al₂O₃ and Au/Al₂O₃ were used (Figure 2). As can be seen from Figure 2, HCHO is an additional product when Pt/Al₂O₃ and Au/Al₂O₃ were used as the catalyst. Despite the clear potential benefits of catalysis reported from this work, data on the identity of the suitable catalyst, species, active and intermediates was not reported and as result, catalysis in plasmas is remains limited. Thus, this work aim to study of non-thermal plasma conversion of CH₄, CO₂ and N₂ in particular the effect of input power and the product present in the plasma using SnO₂ – coated Macor® as potential catalysts. The data obtained were compared to those obtained using uncoated Macor®.

3. Materials and Methods

2.1.1 The Non-thermal plasma cell
Figure 3 shows the schematic of the NTP cell used in this work. The Macor® plate (Goodfellow Cambridge, UK) were covered by a Ti electrode (Dexmet Corp, USA) and a stainless steel electrode (RS Components, UK). The electrodes were connected to a transformer (Hyrite, China) and the input power were controlled using a voltage controller to the HV transformers.

2.1.2 The NTP FTIR System
In-situ FTIR experiments were carried out using an Agilent FTS7000 FTIR spectrometer. The Infrared passed through the plasma generated on the surface of the Macor®/catalyst via in-house built optical bench which consisted of two mirrors to the detector.

2.1.3 The gas delivery system
The feed gasses (N₂, CO₂, and CH₄) were supplied by BOC Industrial gasses, UK. The gasses compositions were controlled using flow meters purchased from Roxspur Measurement & Control Ltd, UK.

2.1.4 Catalysis
SnO₂ nanopowders were prepared by a hydrothermal synthesis heated at 400°C and 700°C adapted from work by Christensen and co-workers in Newcastle [8].

2.1.5 Data Manipulation
The spectra obtained in the NTP experiments are presented as:

\[
A = \log_{10} \left( \frac{S_R}{S_S} \right)
\]

(1.0)

where, Sᵣ is incident light and Sₛ is transmitted light. The concentrations of the products observed in in this work were calculated using the Beer-Lambert law:

\[
A = \varepsilon c L
\]

(2.0)

where: \( \varepsilon \) is the molar decadic extinction coefficient (M⁻¹ cm⁻¹), \( c \) = concentration (M) and \( L \) = optical path length (cm).

The calculation of conversion of CO₂ and CH₄ were adapted using the same method carried out by Christensen et. Al [1-4] and defined as:

\[
%\text{CO}_2 = 100 \times \left( \frac{[\text{CO}_2]_{\text{feed}} - [\text{CO}_2]_{\text{glow}}}{[\text{CO}_2]_{\text{feed}}} \right)
\]

(3.0)

\[
%\text{CH}_4 = 100 \times \left( \frac{[\text{CH}_4]_{\text{feed}} - [\text{CH}_4]_{\text{glow}}}{[\text{CH}_4]_{\text{feed}}} \right)
\]

(4.0)
where $[\text{CO}_2]_{\text{glow}}$ and $[\text{CH}_4]_{\text{glow}}$ is the concentration of CO$_2$ or CH$_4$ in the plasma glow and $[\text{CO}_2]_{\text{feed}}$ and $[\text{CH}_4]_{\text{feed}}$ is that in the feed to the plasma cell.

The percentage of the CO$_2$ or CH$_4$ in the feed gas is defined as:

\[
\%\text{CO}_2 \text{ feed} = \left( \frac{[\text{CO}_2]_{\text{feed}}}{0.0408 \text{ M}} \right) \times 100\%
\]

\[
\%\text{CH}_4 \text{ feed} = \left( \frac{[\text{CH}_4]_{\text{feed}}}{0.0408 \text{ M}} \right) \times 100\%
\]

where 0.0408 M is the concentration of 1 mole of ideal gas at 298 K and 1 atm.

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**Figure 3. Schematic diagram of the NTP cell**

4. Result and Discussion

Figure 4 shows spectra collected using the NTP cell with a gas feed of CO$_2$, CH$_4$ and N$_2$ with SnO$_2$: 700 °C coated Macor® at a total flow rate of 30 cm$^3$ min$^{-1}$ and 24 W input power. The spectrum collected immediately before the plasma was initiated was employed as the reference, $S_R$, and sample spectra were collected every 2 minutes up to 20 minutes, $S_S$. 
As can be seen from Figure 4, no other species being observed other than the loss of CO$_2$ and CH$_4$ and the experiments was repeated at an input power of 20 W, with no additional bands being observed. The feature between 2300 and 2400 cm$^{-1}$ may be attributed to the P and R bands of the CO$_2$ asymmetric stretch ($\nu_3$) fundamental absorption [9,10] and the features between 3500 and 4000 cm$^{-1}$ are CO$_2$ combination bands ($\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$) [11]. Figure 5 shows a plot of the absorbances of the CO$_2$ combination band at 3625 cm$^{-1}$ and CH$_4$ band at 3085 cm$^{-1}$ as a function of time, and Figure 6 shows the analogous plots normalized to their maximum values. As can be seen in Figures 5 and 6, the CH$_4$ and CO$_2$ loss features increase in intensity with time and the reduced intensities of the CH$_4$ Q branches suggest that CH$_4$ and CO$_2$ are simply being rotationally excited in the plasma [1, 3, 7]. The CO absorbance at 2176 cm$^{-1}$ did not be discernible in Figure 4 and CO may have been produced but the reduced pathlength of the cell resulted in an absorbance below the detection limit. Rotationally-excited CO$_2^*$ observed in Figure 4 may be formed directly through collisions with electrons in the plasma [12,13] via:

$$\text{CO}_2 + e^- \rightarrow \text{CO}_2^*(\Sigma^+) + e^- \quad (7.0)$$

or via collisional energy transfer from vibrationally excited species such as N$_2^*$($\Sigma^+$) [13]:

$$\text{CO}_2 + \text{N}_2^*(\Sigma^+) \rightarrow \text{CO}_2^*(\Sigma^+) + \text{N}_2 \quad (8.0)$$

whilst CO$_2^*$($\Sigma^+$) decay can take place through relaxation to CO$_2$ and photon emission or dissociation into CO and atomic oxygen [14,15]:

$$\text{CO}_2^*(\Sigma^+) \rightarrow \text{CO} + \text{O} \quad (9.0)$$

$$\text{O} + \text{O} \rightarrow \text{O}_2 \quad (10.0)$$
Figure 5. Plots of the absorbance of the CO₂ at 3625 cm⁻¹ and CH₄ at 3085 cm⁻¹ from the experiment in fig. 4 as a function of time.

Figure 6. Plots of the normalised absorbance in Figure 4 as a function of time.

Figure 7 compares the spectrum collected after 20 minutes in Figure 4 to that collected in an analogous experiment using SnO₂ 400 °C coated Macor® under the same experimental conditions. As can be seen from Figure 7, SnO₂ 400 °C coated Macor® in the NTP cell resulted in no observed products, even at higher input power and with different calcination temperature and the result somewhat different with uncoated Macor®. Based on the literature [10, 16, 17], the gained features in Figure 7 can be summarised in Table 1 below.
Table 1. Summary of the gained features in Figure 7

| Wavenumber | Assignments                        | References |
|------------|-----------------------------------|------------|
| 2880 cm⁻¹  | asymmetric C-H stretch            | [16] [10]  |
| 1655 cm⁻¹  | amide I (C=O stretch)             | [3] [10]   |
| 1512 cm⁻¹  | amide II (N-H in plane deformation)| [7]        |
| 2152 cm⁻¹  | ketene                            | [10] [17]  |
| 2210 cm⁻¹  | C₅O₂                              | [10] [17]  |

Interestingly, as can be seen from Figure 7, Macor® has a direct catalytic influence on the production of ketene, acetamide and C₅O₂ in addition to unreacted but rotationally-excited CO₂ and CH₄ and proving that SnO₂ is inactive in NTP and hence inhibited that of Macor® when employed as coating.

Figure 7. In-situ FTIR spectra collected after 20 minutes operation with plasma at an input power of 24 W. The gas compositions were: (i) 9% CO₂ + 22% CH₄ + 69% N₂, (ii) 9% CO₂ + 26% CH₄ + 65% N₂ and (iii) 3% CO₂ + 9% CH₄ + 88% N₂ at a total flow rate of 30 cm³ min⁻¹. The spectra were moved up by the absorbances shown in order to facilitate comparison.

5. Conclusions
No reaction taking place in NTP experiments on SnO₂ coated Macor® even with different calcination temperature, whereas a number of by products were observed in the NTP experiment of uncoated Macor®. Macor® proved to be unexpectedly active for the conversion of CH₄, CO₂ and N₂ and the data gained in this work clearly showing catalyst selection for NTP is critical and selectivities of the products were different depending on the selection of the catalyst.

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References
[1] Christensen, P.A., Abd Halim bin Md Ali, Mashhadani, Z.T.A.W. et al. A direct fourier transform infrared spectroscopic comparison of the plasma- and thermally-driven reaction
of CO$_2$ at Macor. Plasma Chem Plasma Process (2018) 38: 293

[2] Christensen, P.A., Mashhadani, Z.T.A.W., Abd Halim bin Md Ali et al. In-situ FTIR studies on the oxidation of isopropyl alcohol over SnO$_2$ as a function of temperature up to 600 °C and a comparison to the analogous plasma-driven process. Physical Chemistry Chemical Physics (2018) 20: 9053-9062.

[3] Christensen, P.A., Abd Halim bin Md Ali, Mashhadani, Z.T.A.W. et al. The production of ketene and C$_5$O$_2$ from CO$_2$, N$_2$ and CH$_4$ in a non-thermal plasma catalysed by earth-abundant elements: an in-situ FTIR study. Plasma Chem Plasma Process (2018) 38: 461.

[4] Christensen, P.A., Mashhadani, Z.T.A.W., Abd Halim bin Md Ali et al. The production of methane, acetone, “cold” CO and oxygenated species from isopropyl alcohol in a non-thermal plasma: an in-situ FTIR study. Journal of Physical Chemistry A (2018) 122 (17), 4273-4284.

[5] Li, W., Y. Yanhui, W. Chunfei, G. Hongchen, and T. Xin, One-step reforming of CO$_2$ and CH$_4$ into high-value liquid chemicals and fuels at room temperature by plasma-driven catalysis. Angewandte Chemie International Edition, 2017. 56(44): p. 13679-13683.

[6] Bogaerts, A. and E.C. Neyts, Plasma technology: An emerging technology for energy storage. ACS Energy Letters, 2018. 3(4): p. 1013-1027.

[7] A.H.M.Ali (2018), In-situ FTIR studies of the plasma glow region of catalysed non-thermal plasmas [Doctoral Dissertation, Newcastle University], Newcastle University, United Kingdom.

[8] P. A. Christensen, P.S.A., R. G. Egdell, S. Maneelok and D. A. C. Manning, An in situ FTIR spectroscopic and thermogravimetric analysis study of the dehydration and dihydroxylation of SnO$_2$: the contribution of the (100), (110) and (111) facets. Physical Chemistry Chemical Physics, 2016. 18(33): p. 22990-22998.

[9] Herzberg, G., Molecular spectra and molecular structure Vol. Vol.2: Infrared and Raman spectra of polyatomic molecules. 1945, New York Van Nostrand Reinhold.

[10] Stein, S.E. "Infrared Spectra" in NST Chemistry Webbook, NIST Standard Reference Database Number 69. [cited 2017 September 5]; Available from: http://webbook.nist.gov/cgi/cbook.cgi?Contrib=MSDC-IR.

[11] Bennett, C.J., C.S. Jamieson, and R.I. Kaiser, Mechanistical studies on the formation and destruction of carbon monoxide (CO), carbon dioxide (CO$_2$), and carbon trioxide (CO$_3$) in interstellar ice analog samples. Physical Chemistry Chemical Physics, 2010. 12(16): p. 4032-4050.

[12] Gordillo-Vázquez, F.J., Air plasma kinetics under the influence of sprites. Journal of Physics D: Applied Physics, 2008. 41(23): p. 234016.

[13] Rond, C., A. Bultel, P. Boubert, and B.G. Chéron, Spectroscopic measurements of nonequilibrium CO$_2$ plasma in RF torch. Chemical Physics, 2008. 354(1): p. 16-26.

[14] Earle K. Plyler, Lamdin R. Blaine, and E.D. Tidwell, Infrared absorption and emission spectra of carbon monoxide in the region from 4 to 6 microns. Journal of Research of the National Bureau of Standards 1955. 55: p. 183-189.

[15] Bennett, C.J., C.S. Jamieson, and R.I. Kaiser, Mechanistical studies on the formation and destruction of carbon monoxide (CO), carbon dioxide (CO$_2$), and carbon trioxide (CO$_3$) in interstellar ice analog samples. Physical Chemistry Chemical Physics, 2010. 12(16): p. 4032-4050.

[16] Roeges, N.P.G., A guide to the complete interpretation of infrared spectral of organic structures. 1994: Wiley.

[17] Socrates, G., Infrared and Raman Characteristic Group Frequencies: Tables and Charts. 1980, Chichester: John Wiley and Sons.