Advancing insights of plasma catalysis by *operando* transmission FTIR spectroscopy in a novel water-cooled DBD cell

J. Van Turnhout^{1, 2}, E.J.M. Hensen² and A. Bogaerts¹

 ¹ PLASMANT, Department of Chemistry, University of Antwerp, Antwerp, Belgium
² Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

Abstract: Water-cooled DBD plasma reactors show promising results for direct plasmacatalytic CO₂ hydrogenation into CH₃OH. The effect of water-cooling on (surface) reaction mechanisms is poorly understood. Here, we present a novel water-cooled *operando* transmission FTIR cell that can be applied to study the surface species formed during plasmacatalytic CO₂ hydrogenation, along with the effects of water cooling on the formation of these species and the catalyst surface temperature.

Keywords: Plasma catalysis, water-cooled dielectric barrier discharge, operando FTIR

1. Introduction

CO₂ conversion into value-added chemicals is gaining increased attention as a tool in the fight against climate change. A particularly interesting route is direct CO₂ hydrogenation into CH₃OH. Conventionally, this conversion is done by thermal catalysis, although obtaining high yields remains challenging. While from a thermodynamic point of view the process would benefit from low operating temperatures due to its exothermicity (-50 kJ/mol), the kinetic barriers to activate CO₂ are high. Therefore, typically compromises are made in the choice of reaction conditions (elevated pressure and mild temperature, ~ 50 bar and ~ 200 °C [1].

An alternative approach is the combination of catalysis with non-thermal plasma, i.e., plasma catalysis. For this, dielectric barrier discharges (DBDs) have received great attention, because of their ease of use and operation at ambient pressure and low temperature. The high-energy electrons of the plasma enable the rate-limiting activation of CO_2 , while a low operating temperature is maintained. Thus, plasma catalysis offers a way to enable the kinetically limited process, while maintaining thermodynamically favorable conditions [2].

Thus, direct plasma-catalytic CO₂ hydrogenation has recently attracted interest by several authors. While some authors found a significant improvement in CH₃OH selectivity upon adding a catalyst to a DBD plasma, the yields remain very low, and CO and CH₄ are reported as main reaction products [3-5]. Recently, however, significant improvements were made by Wang et al. [6], who reported a high CH₃OH yield and selectivity of 11.3 % and 53.7 %, respectively. For this, they employed a water-cooled DBD reactor, in which the cooling water is employed as ground electrode. However, there is a lack of understanding about this phenomenon. For instance, it is thus far unclear to what extent the surface chemistry on the catalyst is influenced by the water cooling of the reactor.

To get a better understanding of the surface chemistry in catalytic processes, typically, in thermal catalysis, *in-situ* (i.e., under environments mimicking those encountered during catalysis) spectroscopy is applied. FTIR

spectroscopy is of particular relevance for this, as it allows for the detection of surface species on a catalyst surface [7].

While many *in-situ* and *operando* FTIR setups have been developed for thermal catalysis, the design of similar cells for plasma catalysis has only recently started and has proven to be particularly challenging. Indeed, the main challenge lies in the confinement of the discharge around the catalytic surface, so that the electrodes must be spatially separated from other conductive materials.

Clearly, typical (partly) metallic *in-situ/operando* cells used for thermal catalysis are not suited for plasmacatalytic applications. Therefore, several authors have reported on the development of specific DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) cells for plasma-catalytic application [8-12].

Alternatively, transmission FTIR can be applied. Indeed, the application of transmission FTIR can hold significant advantages over DRIFTS, with the main advantage of the former being a more straightforward (quantitative) interpretation of the obtained spectra [13]. Until recently, application of transmission FTIR in plasma catalysis was limited to (i) low pressure plasma [14, 15] or (ii) closed systems [16], but recently, Van Turnhout et al. [17] reported on a novel *in-situ* transmission FTIR cell used for plasma-catalytic systems under atmospheric pressure and continuous flow.

Still, linking plasma-catalytic activity data, often obtained from packed-bed DBD experiments, to *in-situ* characterization remains a major challenge. To bridge this gap, *operando* (simultaneously collecting catalyst characterization and online product analysis data under relevant reaction conditions) spectroscopy is of particular interest [7]. A transition from *in-situ* to *operando* operation is however not straightforward, as it does not suffice to connect an online product analysis to existing *in-situ* cells. Indeed, to operate under true *operando* conditions, and thus obtain a straightforward link between catalyst activity and surface characterization, the cell must be subject to strict criteria, e.g., a low dead volume, a high reproducibility, and a uniform temperature profile [7].

Below, we present a novel transmission FTIR cell that is specifically designed for plasma-catalytic application and

meets these strict criteria. Moreover, the design of the cell incorporates the possibility of water-cooling of the ground electrode during operation.

2. Cell design

As discussed above, *operando* FTIR cells are subject to strict criteria. In thermal catalysis, a prime example of a cell that meets these criteria is the *sandwich* cell developed by LCS Caen [18]. As it is almost entirely metallic, it is obviously not suitable for use in plasma-catalytic systems. Therefore, we designed a cell with a cross-section inspired by the *sandwich* cell but adapted for plasma-catalytic application.



Fig. 1. General overview of the insides of our PEEK cell showing the plasma chamber (1) with pellet holder (2) and the water chamber (3). PEEK is illustrated in beige, while ZnSe windows are colored yellow.

Our new cell (Figure 1), which is manufactured from polyether ether ketone (PEEK), consists of two separate chambers: (i) the plasma chamber, and (ii) the water chamber. First, the plasma chamber (Figure 2) is enclosed by two ZnSe windows, one of which forms the outside of the cell, while the other functions both as the separation between both chambers and the dielectric barrier. It is equipped with a pellet holder, which houses both the high voltage (HV) electrode (Au mesh, 0.004 mm thickness; connection through Cu wire) and the catalyst pellet (~ 10 mg). All parts are assembled in a fixed position to ensure reproducibility. The total gas volume of the cell is limited to ~ 0.25 mL, and solely centred around the catalyst pellet to minimize the dead volume.

Second, the water chamber (Figure 3) is enclosed by two ZnSe windows, one of which is shared with the plasma chamber, functioning as dielectric barrier, the other one forming the outside of the cell. Right next to the dielectric barrier, the ground electrode (Au mesh, 0.004 mm thickness, connection through Cu foil and wire) is positioned. A small water chamber is created by a PEEK spacer (0.200 mm thickness), allowing for water-cooling of the ground electrode. This small thickness is essential to ensure sufficient IR transmission. To extend the transmission window in relevant wavenumber regions (i.e., relevant for surface species, typically ~ 3200 - 2800 cm⁻¹ for e.g., CHx and formates, and 2200 - 1200 cm⁻¹ for e.g., carbonyls, formates, and carbonates), we apply D₂O for cooling instead of H₂O (Figure 4).



Fig. 2. Cross-section of our PEEK cell showing the plasma chamber with gas inlet (1), gas outlet (2), catalyst pellet (3) and the electrode connector inlet (4). Not shown is the HV electrode, which is positioned behind the catalyst pellet.



Fig. 3. Cross-section of our PEEK cell showing the water chamber with water inlet (1), water outlet (2), the electrode connector inlet (3), and the PEEK spacer (4). Not shown is the ground electrode, which is positioned on top of the ZnSe window.



Fig. 4. Transmission spectra of the PEEK cell with the water chamber filled with H₂O (blue) and D₂O (grey), showing a broad transmission window in relevant regions when D₂O is used.

3.Applications

First, our novel cell can be used to monitor the effect of water-cooling of the ground electrode on the surface temperature. Indeed, while the effects of water-cooling of the ground electrode on plasma alone have been explored by Duan et al. [19], to the best of our knowledge, the implications of these effects on surface temperature of a catalyst sample are unexplored. Specifically, we will monitor the temperature of a BaSO₄ pellet inside our operando cell as a function of the water-cooling of the ground electrode. Indeed, as described in our earlier work [17], BaSO₄ presents absorption bands at intensities near 2000 cm⁻¹, showing a bathochromic shift with increasing surface temperature (Figure 5 [17]). Combined with electronic characterization, this will allow us to elucidate the effect of water-cooling on both the plasma characteristics and the sample surface temperature.

Moreover, the specific design of our cell, along with the presence of product monitoring through a gas chromatograph, allows us to study plasma-catalytic systems under *operando* conditions, either with or without water-cooling. First, we will study Cu/SiO₂, with SiO₂ selected as an inert support, to focus on surface species formed on Cu. We will also study Cu/Al₂O₃, as this has been shown to effectively increase the selectivity towards CH₃OH [6] in a water-cooled DBD. Moreover, we will study Cu/CeO₂ to monitor the possible role of oxygen vacancies on CH₃OH formation. Results are in progress.

4. Conclusion

While water-cooled DBDs show promising results for direct CO_2 hydrogenation into CH_3OH , the underlying mechanisms are poorly understood. *In-situ/operando* FTIR spectroscopy can play a major role in elucidating the role of water-cooling on plasma-catalytic (surface) reaction mechanisms, but, as yet, its application is limited due to the complexity of required experimental systems. We propose a new, spatially restricted *operando* transmission FTIR cell for plasma-catalytic application, which allows for water-cooling of the ground electrode during plasma operation, thus allowing for elucidation of the effect of water-cooling on (surface) reaction mechanisms.

5. References

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Fig. 5. Wavenumber of the BaSO₄ band used to probe the BaSO₄ temperature in a H₂/Ar DBD plasma as a function of time. The intensity of the background color is indicative of the applied voltage, going from grey (0 kV, plasma off) to dark red (50 kV). From [17].

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