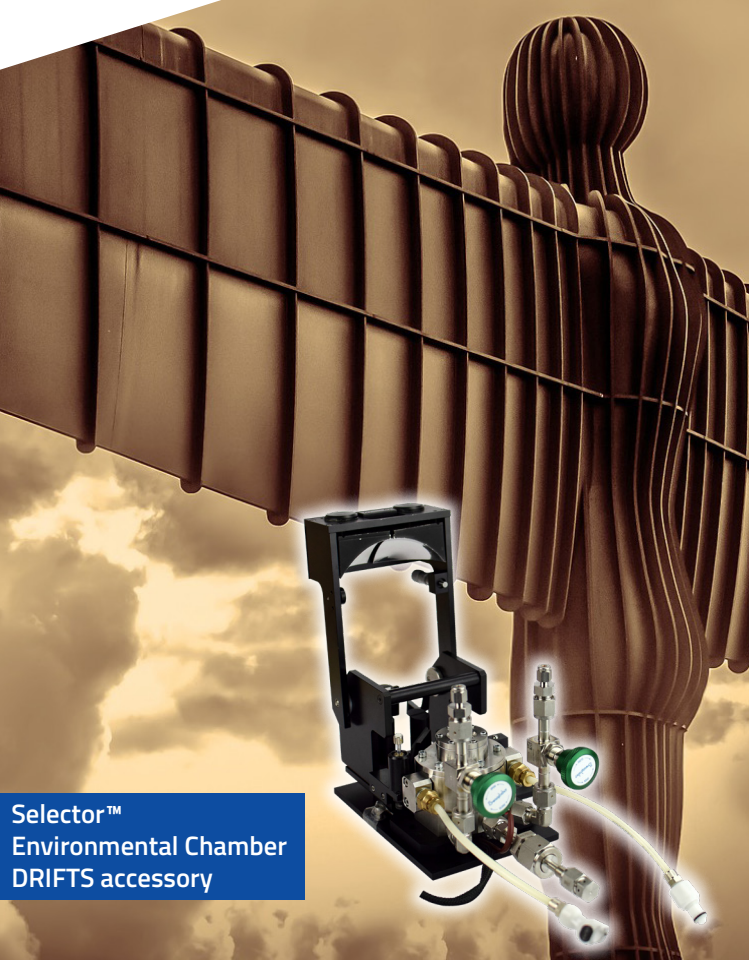


# *Specac*

## Application Note

Investigating the dehydrogenation reaction of IPA over  $\text{CeO}_2$  catalysts with the Selector and Environmental Chamber DRIFTS Accessory



Selector™  
Environmental Chamber  
DRIFTS accessory

# INSIDE: Discover how the Selector has been by one of our customers to yield new insights into novel chemical methods with industrial applications.

## Introduction

Non-thermal plasma generates radicals, ions, and vibrationally and electronically excited species that are not usually present in thermal equilibrium at room temperature [1,2]. Non-Thermal Plasma (NTP) chemistry is an emerging field with the potential to revolutionise the chemical industry through the development of new chemicals and novel methods of greener production for existing ones. Understanding the mechanistic details of the reactions that take place on the surface of the NTP exposed catalyst is critical in developing this technique to the point where it is suitable for industrial deployment. FTIR spectroscopy is a proven technique that is suitable for probing these intermediate species. Once the fundamentals are understood this can then feed through into next generation catalysts which have been designed to promote the chemistries that go on in these systems.

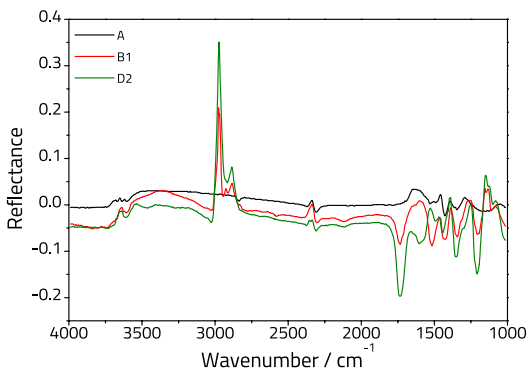
As part of their larger study into the reaction of IPA on Ceria catalysts to form acetone and acetylaldehyde Christensen *et al.* used the Selector and environmental chamber to understand the types of adsorbates present on the catalyst surface at different temperatures and contrasted these to the chemistries that were observed in their home built FTIR plasma chamber. This application note will summarise a part of their study.

### Selector™ Environmental Chamber

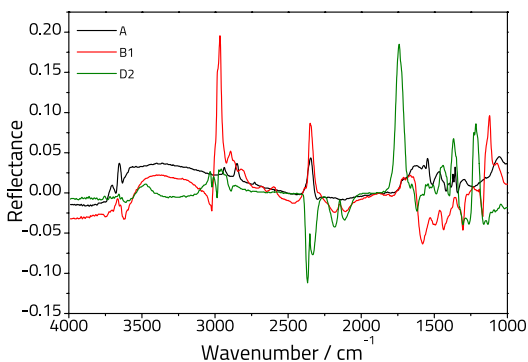
- Environmentally sealed reaction chamber for in-situ diffuse reflection studies
- Temperature range ambient to 800 °C (under vacuum)
- Maximum pressure 500 psi; vacuum 0.001 Torr
- Safety features including pressure certified ZnSe windows and 'burst disc' overpressure device
- Works with the Selector™ diffuse reflectance accessory

## Acknowledgement

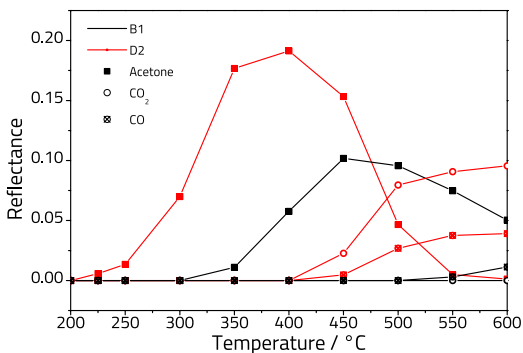
This application note is adapted from [3], with permission from Professor Paul Christensen, Newcastle University.



**Figure 1:** Spectra recorded for the samples A (under  $N_2$ ), B1 and D2 (under 5% IPA/ $N_2$ ) at 400 °C minus the spectrum recorded at 250 °C. Adapted from [3], Figure 3c.



**Figure 2:** Spectra recorded for the samples A (under  $N_2$ ), B1 and D2 (under 5% IPA/ $N_2$ ) at 600 °C minus the spectrum recorded at 400 °C. Adapted from [3], Figure 3d.



**Figure 3:** Plots of the reflectances at the peak maxima of the various features, using samples B1 and D2, as a function of temperature between 250 and 600 °C. In each case, the spectra collected at 200 °C were subtracted from those at higher temperature. Adapted from [3], Figure 4.

## Experimental

*In-situ* FTIR experiments were carried out in an Environmental Chamber fitted with a Selector DRIFTS unit on a commercially available spectrometer. For the samples labelled A and B1, CeO<sub>2</sub>/KBr was prepared at a ratio of 1:4 and loaded into the sample holder. Sample D2 was the same except a pure CeO<sub>2</sub> mix was used. During each experiment the environmental chamber was sealed with a static environment of either N<sub>2</sub> (A) or 5% IPA/N<sub>2</sub> (B1 & D2). Sample D2 was pretreated by first heating at 600 °C under N<sub>2</sub> with a 2 hr hold. The sample was cooled to room temperature and kept under flowing N<sub>2</sub> for 3 days and then further treated by heating to 600 °C under a static atmosphere of 5% IPA/N<sub>2</sub> before again cooling to room temperature to begin the experiment.

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## Results and Discussion

The CeO<sub>2</sub> was heated in the environmental chamber under an inert environment (N<sub>2</sub>) from 25-600 °C to investigate the initial adsorbates (Sample A). The DRIFTS spectra identified the presence of hydroxy and carbonate on the catalyst. Physisorbed CO<sub>2</sub> was also observed at all temperatures. As the sample is heated the surface species are redistributed with some evidence for conversion of the carbonates into different forms and/or CO<sub>2</sub>.

The experiment was then repeated twice with the catalyst exposed to IPA: once with a catalyst with no pretreatment (sample B1) and once with a catalyst that was pretreated (Sample D2). FTIR difference spectra (Fig 3(a) in [3]) reveal that, as the samples are heated to 100 °C, B1 behaves similarly to A. D1 on the other hand does not demonstrate interchange between carbonaceous species, and shows a marked difference in the CeO-H region. Relative to the spectrum recorded at 25 °C, the spectrum recorded at 100 °C shows a loss of physisorbed IPA for both B1 and D2.

Figure 1 shows the difference spectra of the 3 samples recorded at 250 °C subtracted from the spectra at 400 °C. It is important to note that in this instance difference spectra have been created by taking one reflectance spectrum away from another, hence positive peaks show the loss of a species, whilst negative peaks show a net gain of a species. For the sample with no IPA (black trace) there are minimal changes evident between these two temperatures. For samples B1 and D2 (red and blue traces) several additional peaks are present.

Loss features at 3647, 2980, 1152, 1130 and 950 cm<sup>-1</sup> are assigned to the loss of IPA in the gas phase. The appearance of a carbonyl band at 1737 cm<sup>-1</sup> shows the formation of acetone, along with other peaks at 1363, 1226, 1215 and 1205 cm<sup>-1</sup>.

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Comparing the samples B1 and D2 it is evident that there is a greater loss of IPA, and a corresponding higher formation of acetone for the sample with a pretreated catalyst (D2).

At higher temperatures additional features are observed in the spectra, as shown in Figure 2, showing the spectra at 600 °C minus the one at 400 °C. Samples A and B1 both show a strong loss peak from physisorbed CO<sub>2</sub> at 2340 cm<sup>-1</sup>. The resultant gas phase CO<sub>2</sub> is too weak to be observed. The spectra of the pretreated sample D2 shows the appearance of gas phase CO<sub>2</sub> at this temperature. Sample B1 shows no change in the carbonyl region indicating a consistent amount of acetone present between 400 and 600 °C. On the other hand, D2 shows a strong loss feature in the carbonyl region indicating a loss of acetone. Both B1 and D2 show evidence for the formation of gas phase CO and CH<sub>4</sub>.

The formation of acetone, CO and CO<sub>2</sub> on B1 and D2 is shown in Figure 3 against temperature. As can be seen acetone formation occurs at a lower temperature for the pretreated D2 sample, with a maximum peak intensity at 400 °C. Sample B1 reaches a maximum at 450 °C. At higher temperatures the peak intensity of acetone declines slightly for B1 up to 600 °C. For the pretreated catalyst the decline occurs at a significantly faster rate with virtually no acetone by 550 °C. For sample D2 the decrease of acetone occurs concurrently with formation of CO and CO<sub>2</sub> suggesting that the acetone is oxidised further. Likewise with sample B1 the slight decline in acetone corresponds to a slight formation of CO.

The differences between the unpretreated and pretreated catalyst can be explained due to presence of carbonate species blocking the active sites of the catalyst. This delays the onset of acetone formation and its subsequent reduction until the carbonates are removed at higher temperatures.

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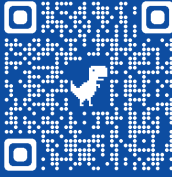
## Conclusion

The thermal reaction of IPA on CeO<sub>2</sub> catalysts has been investigated over a range of temperatures using the Selector™ Environmental Chamber accessory from Specac. The study by Christensen *et al.* clearly demonstrates the critical dependence of reaction parameters on the presence or absence of blocking carbonates on the catalyst surface, which can be controlled by careful treatment of the catalyst.

## References

- [1] Whitehead, J.C., *J. Phys. D Appl. Phys.*, **49**, (2016), 243001 DOI: 10.1088/0022-3727/49/24/243001
- [2] Aerts, R., Martens, T., Bogaerts, A., *J. Phys. Chem. C*, **116**, (2012), 23257–23273 DOI: 10.1021/jp307525t
- [3] Christensen, P.A., Mashhadani, Z. T. A. W., Abd Halim Bin Md Ali, Manning, D.A.C., Carroll, M.A. and Martin, P.A., *Phys. Chem. Chem. Phys.*, **21**, (2019), 1354–1366 DOI: 10.1039/c8cp05983g

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