

# Specac

## Application Note

Supported Ni catalysts in action:

*operando* infrared spectroscopy unravels CO<sub>2</sub> activation over Ni in Specac's HTHP cell



Specac HTHP cell

# INSIDE: *in-situ* reduction and FTIR analysis of Ni catalysts using a High Temperature / High Pressure cell

## Introduction

The increasing CO<sub>2</sub> concentration in Earth's atmosphere is having an adverse effect on the climate. Power-to-methane strategies, in which green electrons are used to produce methane from CO<sub>2</sub>, can be applied to provide electric grid stability and mitigate CO<sub>2</sub> emissions [1]. Nickel is often considered an active and cost-effective metal catalyst to convert CO<sub>2</sub> into methane using sustainable hydrogen. While the CO<sub>2</sub> hydrogenation reaction is widely studied, the reaction mechanism is still under debate. Operando Fourier transform infrared spectroscopy (FTIR) is a powerful technique to identify surface intermediates during reaction and can thus provide new mechanistic insights. This note will highlight the use of a Specac High Temperature High Pressure (HTHP) cell to study Ni catalysts in action using operando FTIR. An array of Ni catalysts supported on different metal oxides were used to establish trends in catalytic activity and to find spectroscopic activity descriptors [2].

### Advanced High Temperature / High Pressure Cell

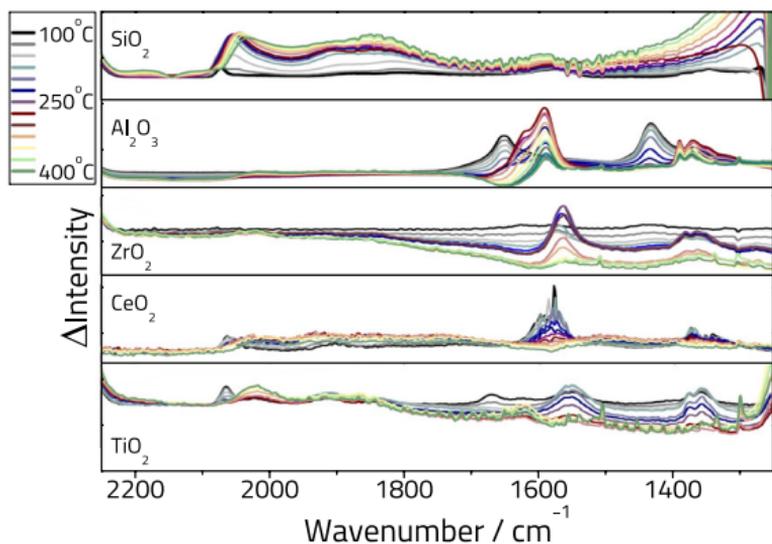
High optical throughput reaction chamber for IR analysis in multiple configurations: transmission, reflectance, and decomposition.

- Sealed sample chamber with controlled atmosphere
- Temperature up to 800 °C / Pressure from vacuum to 68 bar (1000 psi)
- Converts to specular reflectance mode for opaque or reflective samples using external mirrors
- Sample pans allow analysis of gases released from thermal decomposition of solids
- Ideal for characterisation of coal, catalysts, resins/polymers, ceramics, and minerals

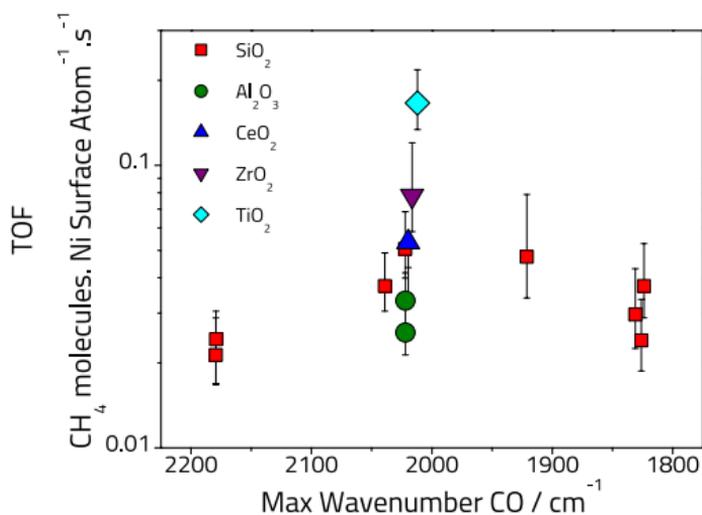
### Author acknowledgement

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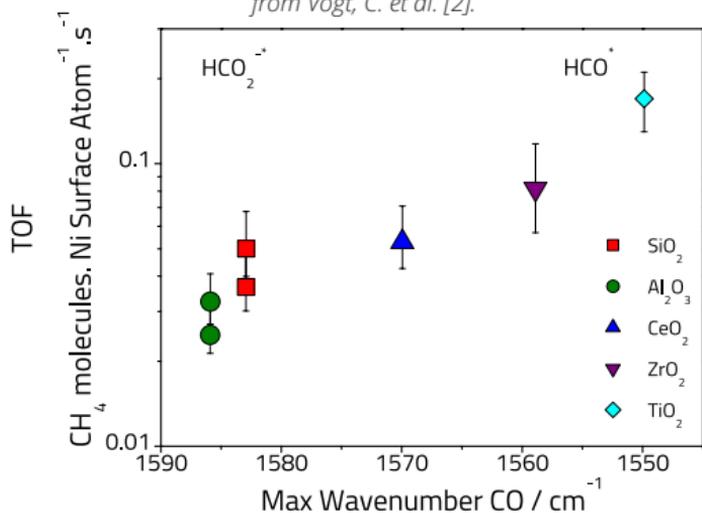
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**Figure 1:** Operando Fourier transform infrared (FT-IR) spectra collected at 100–400 °C during CO<sub>2</sub> hydrogenation (CO<sub>2</sub>:H<sub>2</sub>:N<sub>2</sub>=1:4:5) over Ni catalysts supported on different oxides. The corresponding yield, as measured by a high-throughput reactor system at 300 °C, is displayed at the right. Image reproduced from Vogt, C. et al. [2].



**Figure 2:** Spectroscopic descriptors for the methanation activity of supported Ni catalysts. Showing the wavenumber of the maximum absorbance of adsorbed CO (2200–1800 cm<sup>-1</sup>) plotted against the turnover frequency (TOF) to methane at 400 °C. The different SiO<sub>2</sub> catalysts have different Ni nanoparticle sizes. Image reproduced from Vogt, C. et al. [2].



**Figure 3:** Spectroscopic descriptors for the methanation activity of supported Ni catalysts. Showing the maximum absorbance in the 1590–1540 cm<sup>-1</sup> region plotted against the TOF to methane at 400 °C for Ni on different supports. Image reproduced from Vogt, C. et al. [2].

## Experimental

The investigated catalysts were pressed into 13 mm self-supporting wafers, using a Specac laboratory pellet press with a load of 4 tonnes. The wafer was placed in the Specac HTHP cell. FTIR measurements were recorded with a commercially available spectrometer equipped with a DTGS detector under a wide range of temperatures (100–400 °C) and pressures (1–10 bar). Reaction gases ( $H_2$ ,  $CO_2$ ) and  $N_2$  were allowed in the cell with flows controlled by Bronkhorst mass flow controllers. The product analyses were performed on-line with a gas chromatograph.

## Results and Discussion

Ni catalysts were supported by deposition precipitation on different metal oxides with different degrees of reducibility:  $SiO_2$ ,  $Al_2O_3$ ,  $CeO_2$ ,  $ZrO_2$ , and  $TiO_2$ . All catalysts were reduced in-situ (400–550 °C, depending on the support) before exposure to reaction mixture. Figure 1 shows the FTIR spectra collected at 100–400 °C over the supported Ni catalysts under  $CO_2$  hydrogenation conditions ( $CO_2:H_2:N_2=1:4:5$ ).

Depending on the support used, different spectroscopic features can be observed in the FTIR spectra, as well as differences in the corresponding product distributions. Adsorbed carbonyl species were found on all catalysts in the 2100–1800  $cm^{-1}$  region. The CO species at lower wavenumbers have been assigned to bridged and multi-bound CO respectively. A temperature effect can be observed for linear adsorbed CO, with decreasing CO bond strength at higher temperatures (e.g. from 2060 to 2030  $cm^{-1}$  for Ni/ $SiO_2$ ). Previous work of Vogt *et al.* [3] showed a correlation between the CO vibration strength (an indirect measure for the M-CO strength), and the Ni nanoparticle size (Figure 2). Notably, the effect of the support was an order of magnitude greater than the size effect.

Most of the studied supported Ni catalysts show intense spectral features at wavenumbers below 1600  $cm^{-1}$  associated with adsorbed carbonate, formate, and formyl species. More

reducible supports show a bathochromic shift of signals in the 1590–1540  $\text{cm}^{-1}$  region, which correlate to the increase in turnover frequency (TOF, i.e. intrinsic catalytic activity per Ni surface atom) to methane at 400 °C (Figure 3). The shift of 30–40  $\text{cm}^{-1}$  between the species adsorbed on Ni/SiO<sub>2</sub> and Ni/TiO<sub>2</sub> falls into the expected difference between formate (HCOO-\*) and formyl adsorbates (HCO\*), according to theoretical calculations. It is proposed that the reducible support can delocalize the electrons around adsorbed CO by providing adsorbed hydrogen from the support to the \*CO or \*CO<sub>2</sub>, forming formyl and formate species. According to DFT calculations on model Ni surfaces, this lowers the activation barrier of the rate-determining step and explains the observed higher methanation activity for more reducible supports.

## Conclusion

The HTHP cell was used to collect FTIR spectra of supported Ni catalysts under CO<sub>2</sub> hydrogenation reaction conditions. Differences in spectral features have been highlighted for different catalyst and correlated to catalytic performance. The use of operando spectroscopy has shown to be a powerful tool to investigate industrially relevant catalysts at work and to find vibrational activity descriptors. The knowledge gained can be used to further guide rational catalysts design, in this case looking for catalysts formulations which favor hydrogen transfer between the active phase and the support. The HTHP cell offers a facile way to study a wide variety of catalysts under different reaction conditions, gas compositions, temperatures, and pressures.

## References

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2. Vogt, C. *et al.* Understanding carbon dioxide activation and carbon-carbon coupling over nickel. *Nat. Commun.* 10, 5330 (2019).
3. Vogt, C. *et al.* Unravelling structure sensitivity in CO<sub>2</sub> hydrogenation over nickel. *Nat. Catal.* 1, 127–134 (2018).

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