

## Exploring Opportunities in operando DRIFTS and Complementary Techniques for Advancing Plasma Catalysis

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### Supplementary information

#### S1 Experimental

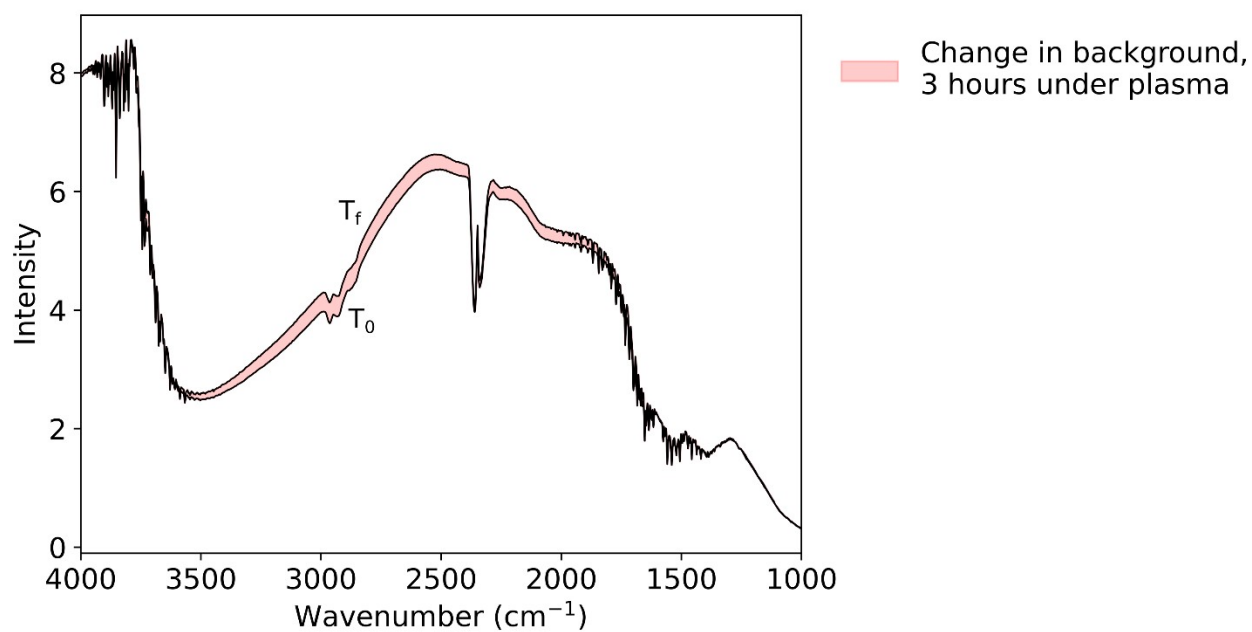
##### S1.1 Catalyst synthesis

The support material used is  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a specific surface area of 185 m<sup>2</sup>/g and a pore volume of 0.43 cm<sup>3</sup>/g (Strem Chemicals, 13-2525). Prior to catalyst synthesis, the support was air-calcined at 823 K for 2 hours at a ramp rate of 2 K/min. The cobalt catalyst on alumina support was prepared through pore-filling incipient wetness impregnation with a 90% volume of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich, > 98%) solution, which was added dropwise to the support with stirring. The mixture was vacuum-dried at 333 K overnight and then calcined in air at 673 K for 2 hours at a ramp rate of 2 K/min in a muffle furnace. The Co metal content in the catalyst was maintained at 15 wt% based on the support.

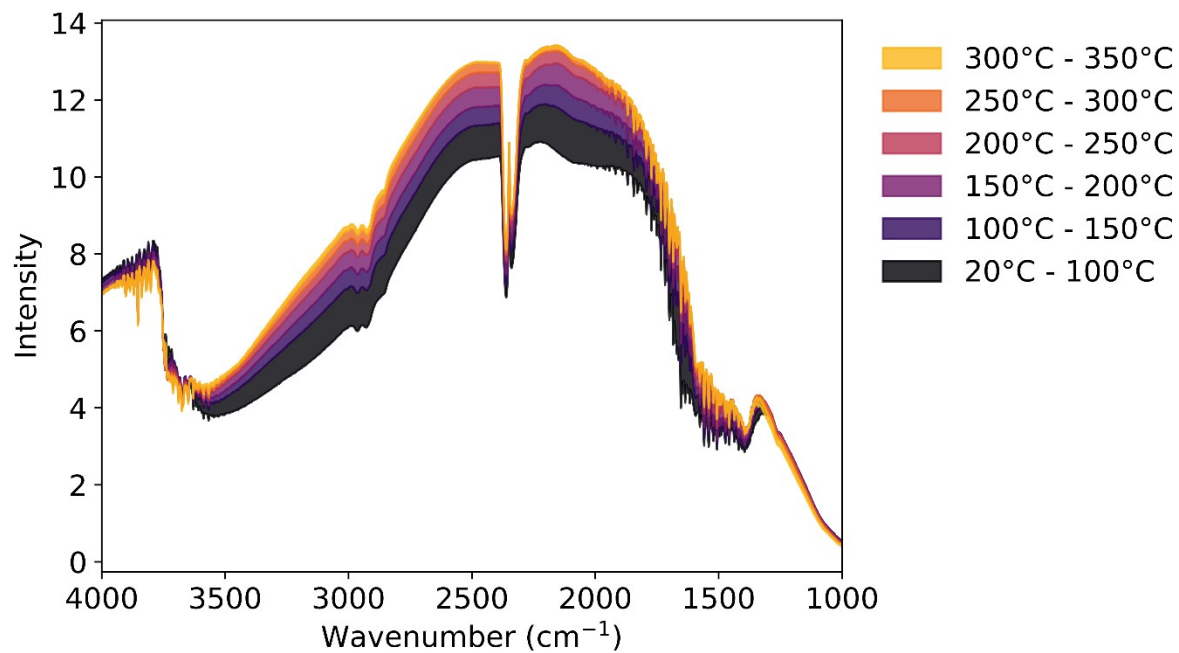
##### S2.2 Plasma *Operando* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (NTP-DRIFTS)

DRIFTS measurements were performed on a Thermo-Nicolet iS50 FTIR spectrometer fitted with a Harrick "Praying Mantis" high-pressure/high-temperature cell equipped with CaF<sub>2</sub> windows. The cell was modified by introducing a high voltage electrode by replacing a cell window. The power electrode consists of a tungsten filament surrounded by a quartz wall. The quartz wall was electrically isolated with a mica sheet to avoid plasma discharge outside the bed. The cell system was grounded. High voltage was generated through an amplifier (Trek 2020/C-HS-L) controlled by an oscilloscope (Tektronix TPS2024) and a function generator (Tektronix AFG2021) generating NTP at an applied frequency of 10 kHz and voltage of 4000 V (AC, peak-to-peak). The catalyst was placed in form of single pellet (2 mm diameter and length) on the ground electrode. Prior to the reaction, the system was purged with 40 sccm of Argon, switching on the plasma source for the NTP tests. For both thermal-only and NTP-assisted tests, the temperature was controlled by a thermocouple (type K) placed on the cell external wall and previously calibrated to control the internal cell temperature at 20, 100, 150, 200, 250, 300 and 350 °C. Background spectra were collected at each temperature under 40 sccm of Ar, with plasma switched on for the NTP experiments. H<sub>2</sub>/CO<sub>2</sub> volume ratio was kept at 3 and the flow diluted in Ar. Initial spectra were collected until steady state was reached. At least 3 sample spectra were then taken for each temperature level.

## S2 Supplementary Figures



**Figure S1:** Background measured for Co/Al<sub>2</sub>O<sub>3</sub> catalyst with plasma at 8000 V and 10 kHz in 40 sccm of Ar. The conditions were maintained for 3 hours at 20 °C. T<sub>0</sub> and T<sub>f</sub> represent the initial and final backgrounds, respectively.



**Figure S1:** Background measured for Co/Al<sub>2</sub>O<sub>3</sub> catalyst with plasma at 8000 V and 10 kHz in 40 sccm of Ar highlighting the temperature impact on background from 20 to 350 °C.