

Supporting Information

Article

Operando CO Infrared Spectroscopy and On-Line Mass Spectrometry for Studying the Active Phase of IrO₂ in the Catalytic CO Oxidation Reaction

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Light path and Temperature Detection

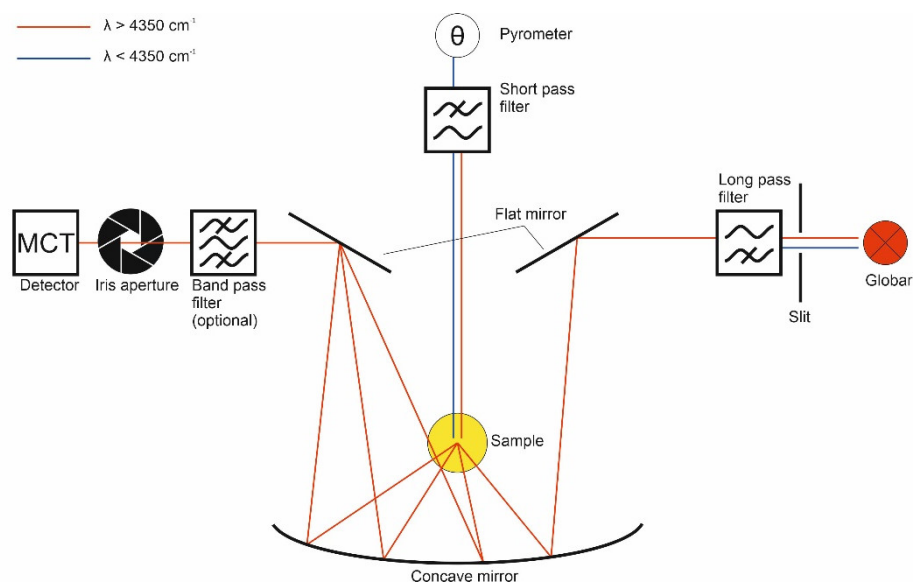


Figure S1. Scheme of the light path through spectrometer and reactor.

Time response of the MS system

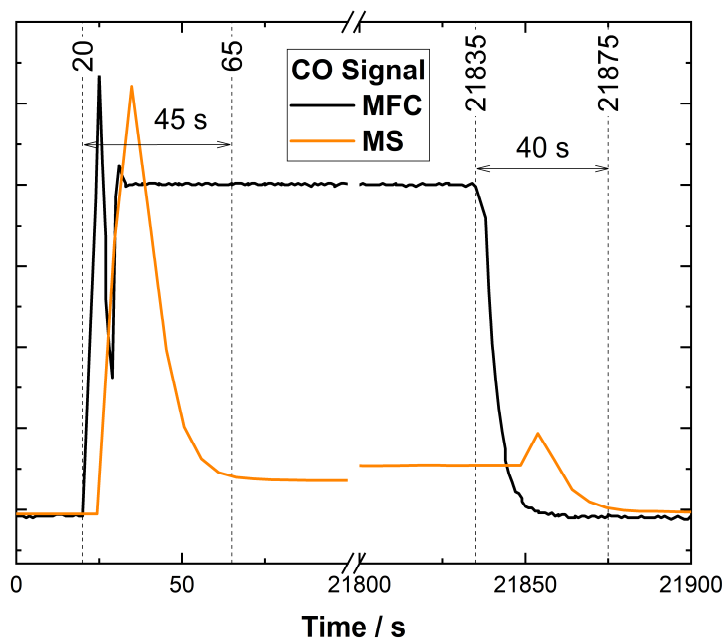


Figure S2. Delay between MFC gas flow and mass spectrometer (MS) signal of CO.

DRIFTS data processing

For all DRIFTS experiments, blank spectra of the catalysts are recorded for every temperature under pure argon conditions during cool down after the pretreatment procedure. Spectra are recorded with 20 scans at 1 cm⁻¹ resolution every 100 s.

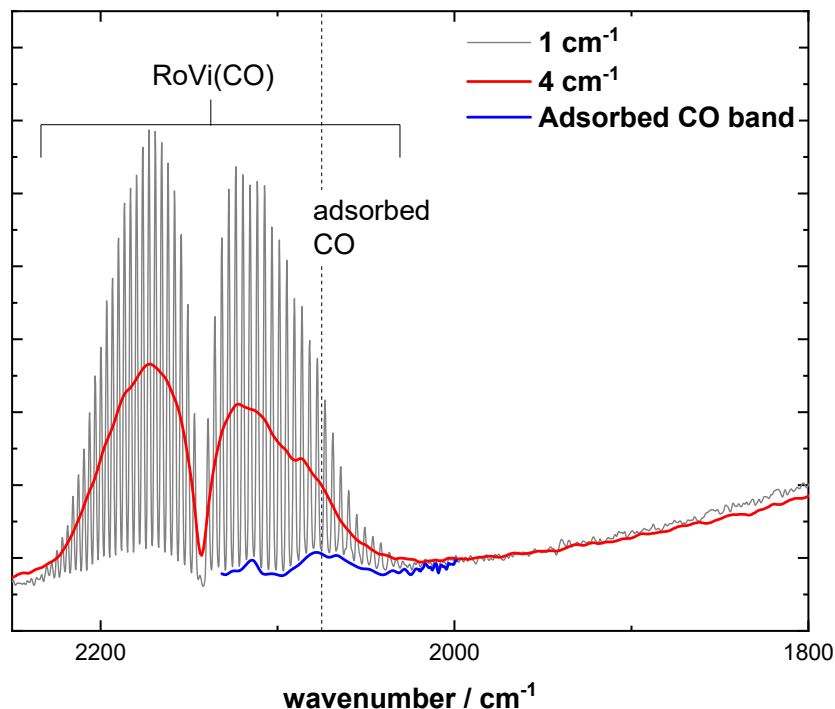


Figure S3. Example of high (1 cm⁻¹) and low (4 cm⁻¹) resolution spectra with adsorbed and gas phase CO bands on IrO₂@TiO₂ at 20 °C under 4% CO. In the 1 cm⁻¹ spectrum (black) the rotational fine structure is resolved allowing for a clear identification of the adsorbed CO band (shown in blue).

The high resolution enables to resolve the rotational fine structure (coupling of rotation with vibration: RoVi spectra) of the gas phase CO band (cf. black spectrum in **Error! Reference source not found.**). The envelope of minima of the RoVi spectrum (blue in **Figure 2**) corresponds to the spectrum without gas phase CO, which allows a clearer view on adsorbed species under reaction conditions that do not show a rotational fine spectrum. If a lower resolution is employed, the RoVi spectrum of gas phase CO appears as two broad bands (cf. red spectrum in **Error! Reference source not found.**) which overlap with the bands of adsorbed CO, thus impeding to resolve adsorbed species (cf. red spectrum in **Error! Reference source not found.**). In CO oxidation experiments the heat of reaction can cause the normalized spectra to be skewed. This is due to the temperature rising more quickly during the spectrum being recorded under reaction conditions (induced by the evolved heat of reaction) than during recording of the background spectrum. This causes a mismatch between background spectrum and reaction condition spectrum. In these cases a linear baseline is subtracted for better visibility of the data.

TEM of IrO₂@TiO₂

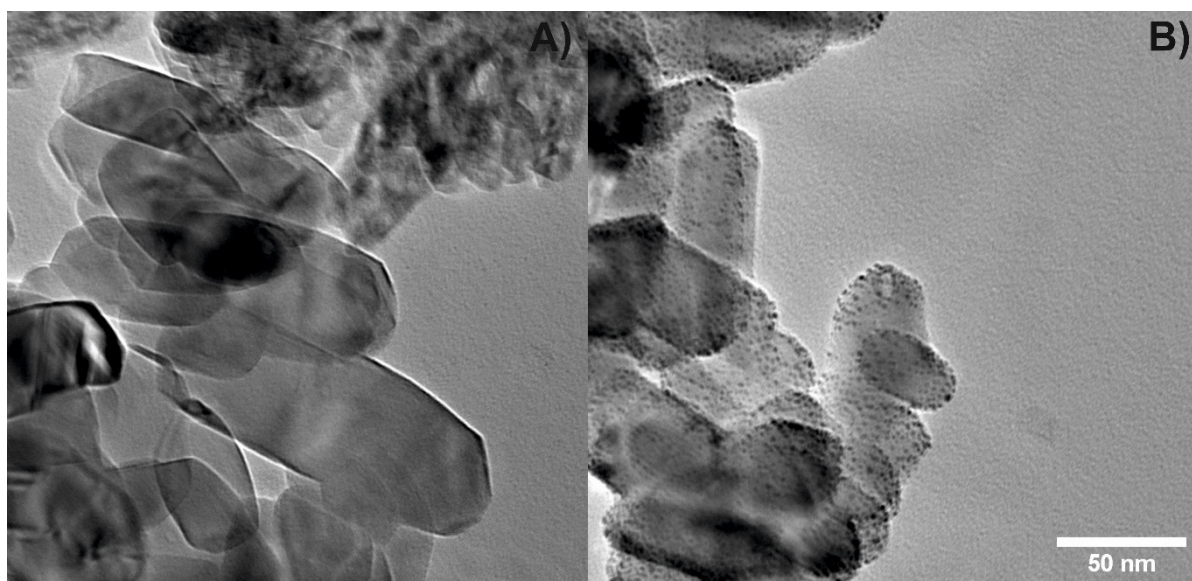


Figure S4. TEM image of A) the pure TiO₂ support and B) IrO₂@TiO₂ at magnification of 81000. The large particles are the TiO₂ support. The dark spots in B) are IrO₂ supported on TiO₂.

XP spectra of incomplete reduction of IrO₂@TiO₂ with H₂

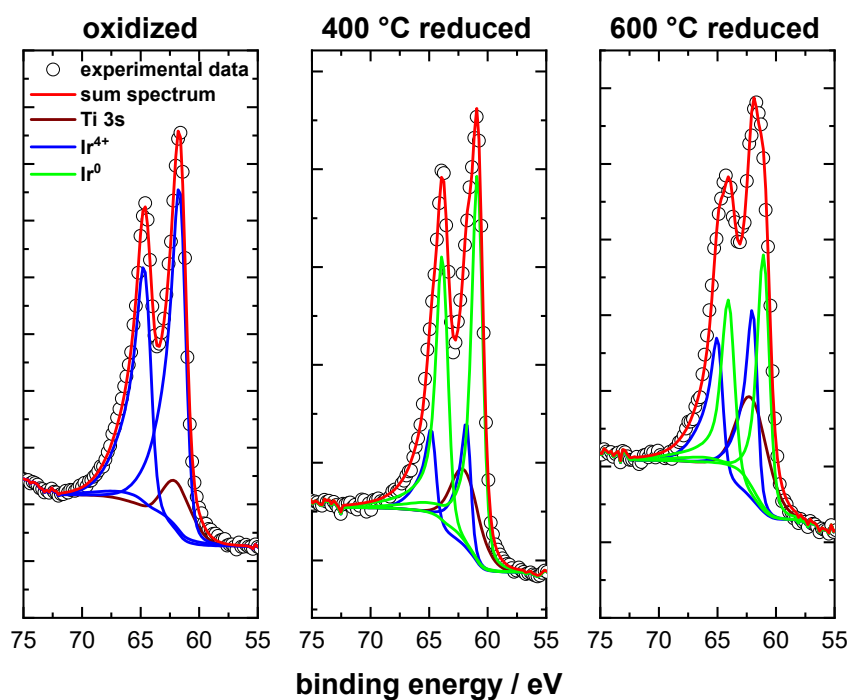


Figure S5. Ir 4f XP spectra of oxidized and reduced IrO₂. The reduced samples were held under the denoted temperature for 24 h.

Raman of Ir⁰ before and after reducing CO oxidation conditions

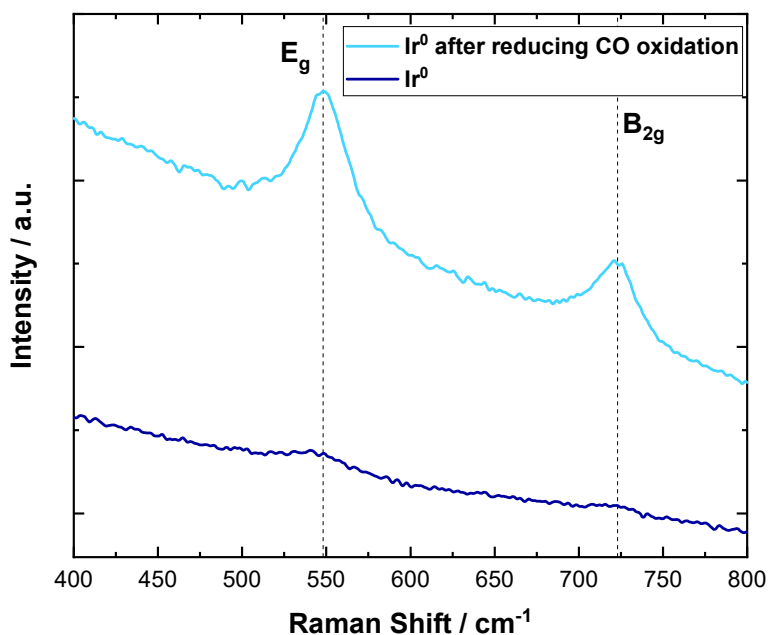


Figure S6. Raman spectra of Ir⁰ before and under reducing (1% O₂/4% CO/95% Ar) reaction feed. One can clearly see the increase of the E_g and B_{2g} bands of IrO₂, demonstrating the oxidation of Ir⁰ under these conditions.

XPS fit parameter and IrO₂@TiO₂ reduction attempts

Table S1. XPS fit parameters.

<i>Species</i>	<i>Peak</i>	<i>Binding energy</i>	<i>FWHM</i>	<i>Fitting parameters</i>
Ir	4f _{7/2}	60.8	1.03	LF(0.6,1,150,300)
	4f _{5/2}	63.8	1.03	LF(0.6,1,150,300)
IrO ₂	4f _{7/2}	61.5	1.30	LF(0.3,1,65,300)
	4f _{5/2}	64.5	1.47	LF(0.3,1,65,300)
TiO ₂	3s	61.9	3.04	GL(30)

The Ir⁰ signal seems to be less after pretreatment at 600 °C, relative to pretreatment at 400 °C. We suspect that at these temperatures the Ir-particles are either overgrown by TiO₂, due to SMSI and/or form a mixed Ir-Ti oxide. We have however not investigated this further.

Blank DRIFT Spectra of rutile-TiO₂ without active component

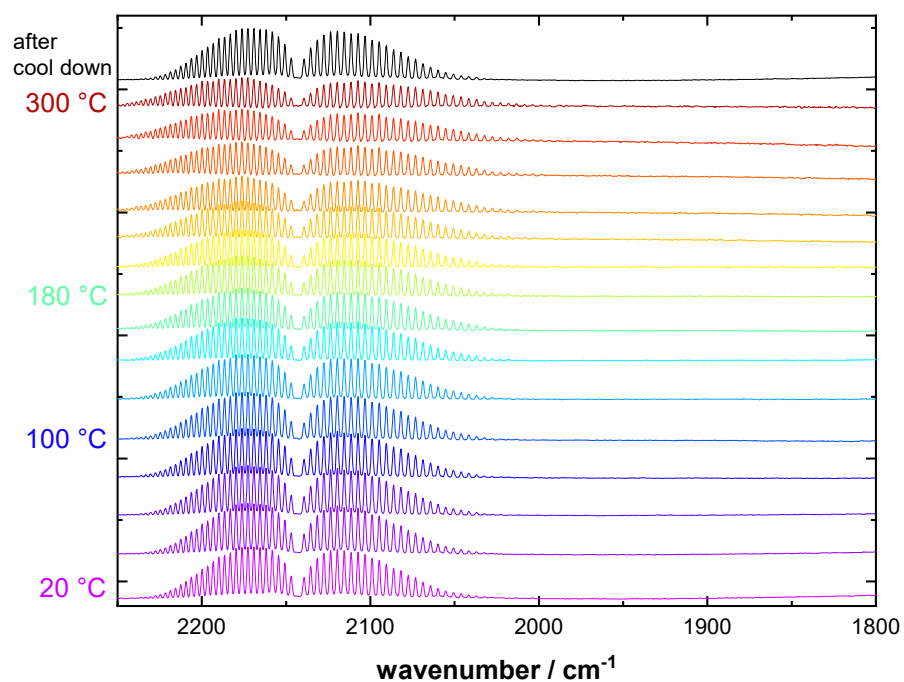


Figure S7. DRIFT spectra of pre-oxidized TiO₂ heated in a CO atmosphere. CO adsorption bands are not observed, while the RoVi fine structure of CO gas appears between 2100-2200 cm⁻¹. The spectrum denoted as “after cool down” was recorded after the sample was cooled back down to room temperature under CO. Temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹.

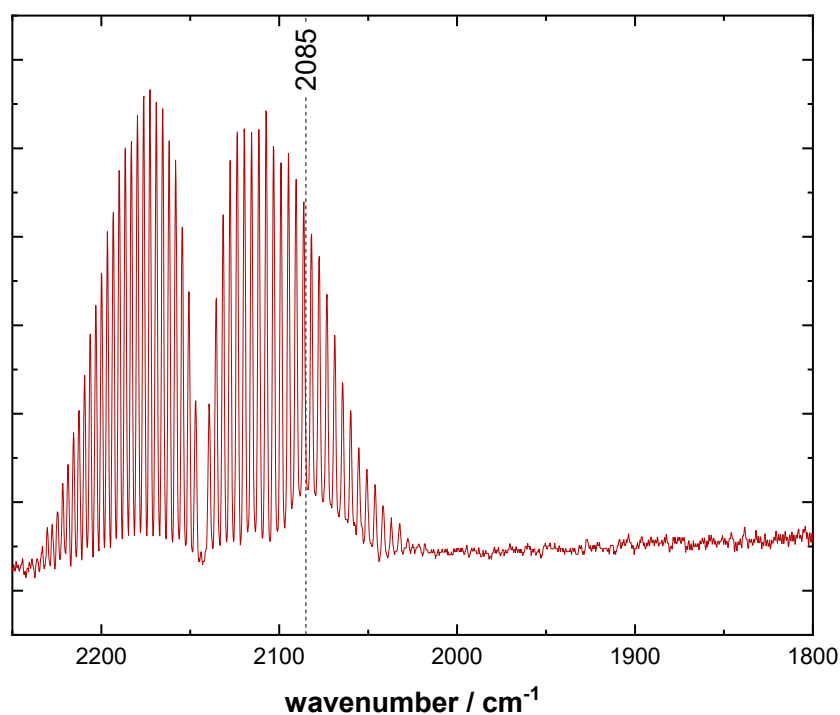


Figure S8. DRIFTS spectrum of CO adsorption on Ir⁰+TiO₂ after oxidative pretreatment under 4% O₂ at 300 °C for 12h. As previously shown for IrO₂@TiO₂ only one band without broad shoulder is observed.