

## Supporting Information

*Article*

# Operando CO Infrared Spectroscopy and On-Line Mass Spectrometry for Studying the Active Phase of IrO<sub>2</sub> in the Catalytic CO Oxidation Reaction

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## Light path and Temperature Detection

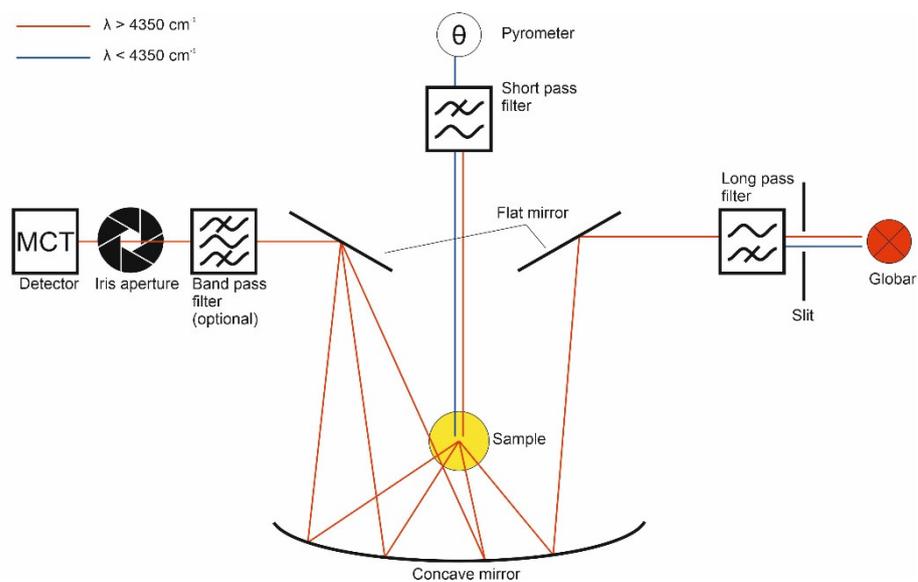


Figure S1. Scheme of the light path through spectrometer and reactor.

## Time response of the MS system

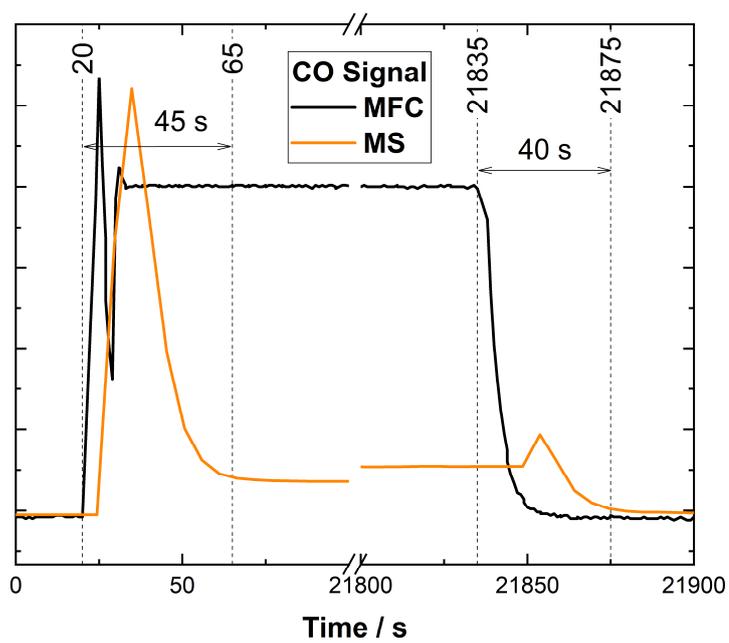
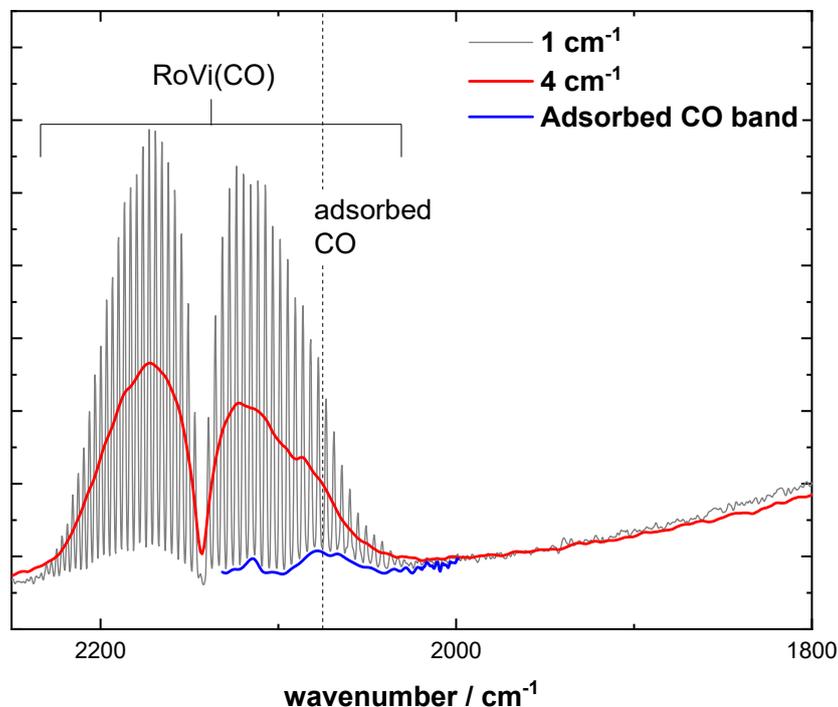


Figure S2. Delay between MFC gas flow and mass spectrometer (MS) signal of CO.

### DRIFTS data processing

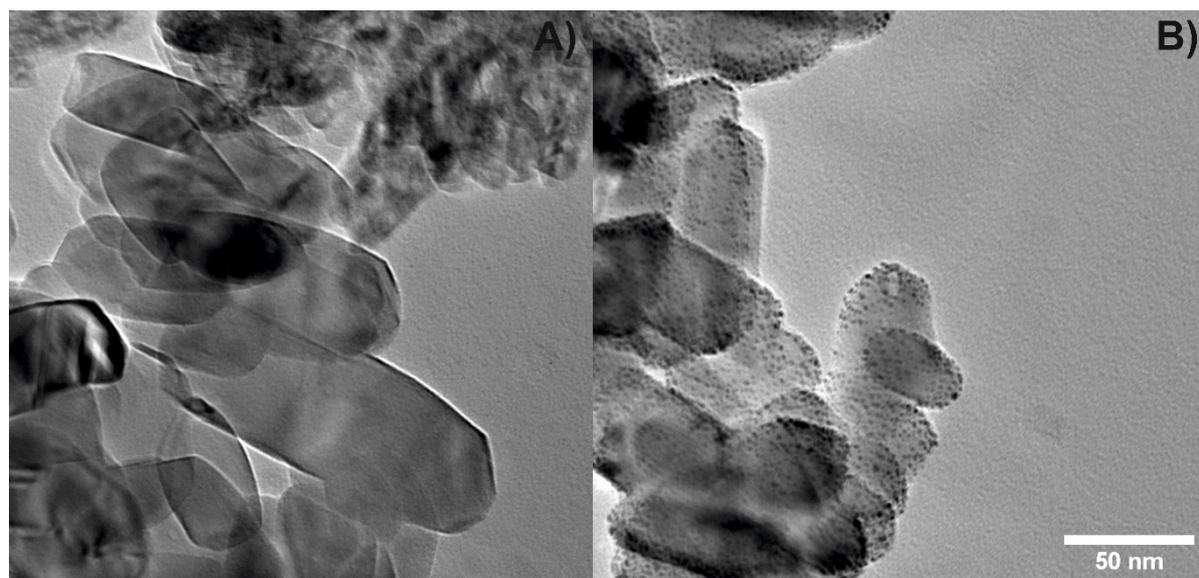
For all DRIFTS experiments, blank spectra of the catalysts are recorded for every temperature under pure argon conditions during cool down after the pretreatment procedure. Spectra are recorded with 20 scans at  $1\text{ cm}^{-1}$  resolution every 100 s.



**Figure S3.** Example of high ( $1\text{ cm}^{-1}$ ) and low ( $4\text{ cm}^{-1}$ ) resolution spectra with adsorbed and gas phase CO bands on  $\text{IrO}_2/\text{TiO}_2$  at  $20\text{ }^\circ\text{C}$  under 4% CO. In the  $1\text{ cm}^{-1}$  spectrum (black) the rotational fine structure is resolved allowing for a clear identification of the adsorbed CO band (shown in blue).

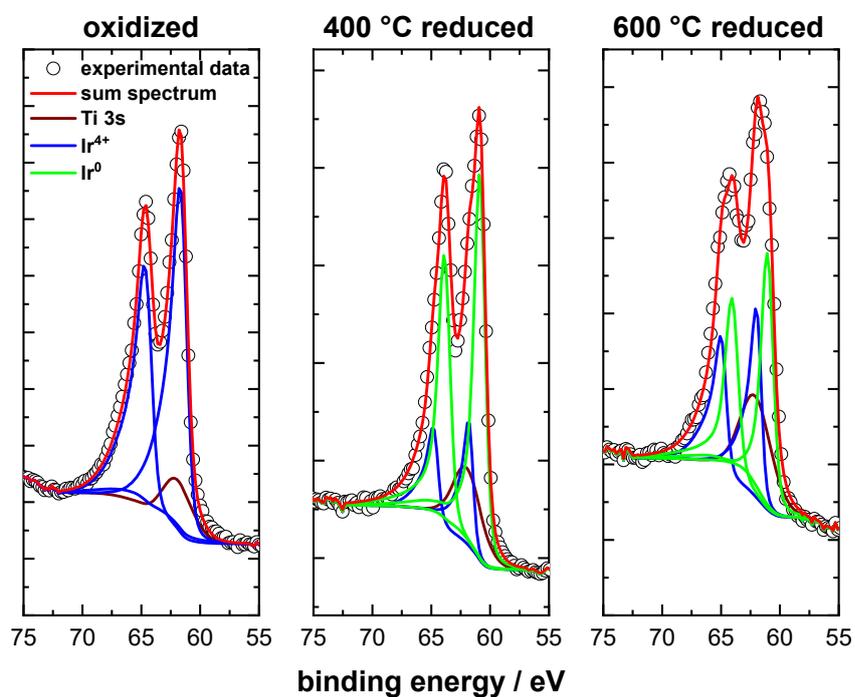
The high resolution enables to resolve the rotational fine structure (coupling of rotation with vibration: RoVi spectra) of the gas phase CO band (cf. black spectrum in **Error! Reference source not found.**). The envelope of minima of the RoVi spectrum (blue in **Figure 2**) corresponds to the spectrum 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 IrO<sub>2</sub>@TiO<sub>2</sub>



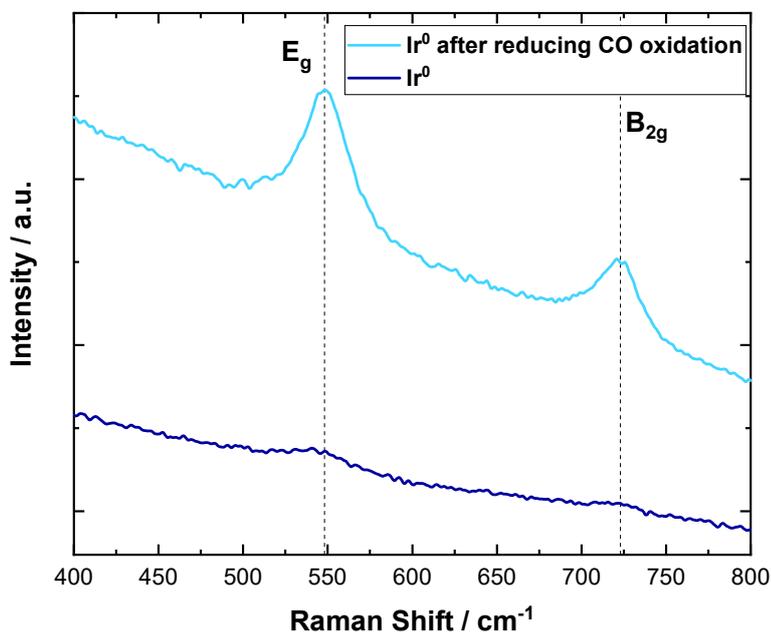
**Figure S4.** TEM image of A) the pure TiO<sub>2</sub> support and B) IrO<sub>2</sub>@TiO<sub>2</sub> at magnification of 81000. The large particles are the TiO<sub>2</sub> support. The dark spots in B) are IrO<sub>2</sub> supported on TiO<sub>2</sub>.

## XP spectra of incomplete reduction of IrO<sub>2</sub>@TiO<sub>2</sub> with H<sub>2</sub>



**Figure S5.** Ir 4f XP spectra of oxidized and reduced IrO<sub>2</sub>. The reduced samples were held under the denoted temperature for 24 h.

## Raman of Ir<sup>0</sup> before and after reducing CO oxidation conditions



**Figure S6.** Raman spectra of Ir<sup>0</sup> before and under reducing (1% O<sub>2</sub>/4% CO/95% Ar) reaction feed. One can clearly see the increase of the E<sub>g</sub> and B<sub>2g</sub> bands of IrO<sub>2</sub>, demonstrating the oxidation of Ir<sup>0</sup> under these conditions.

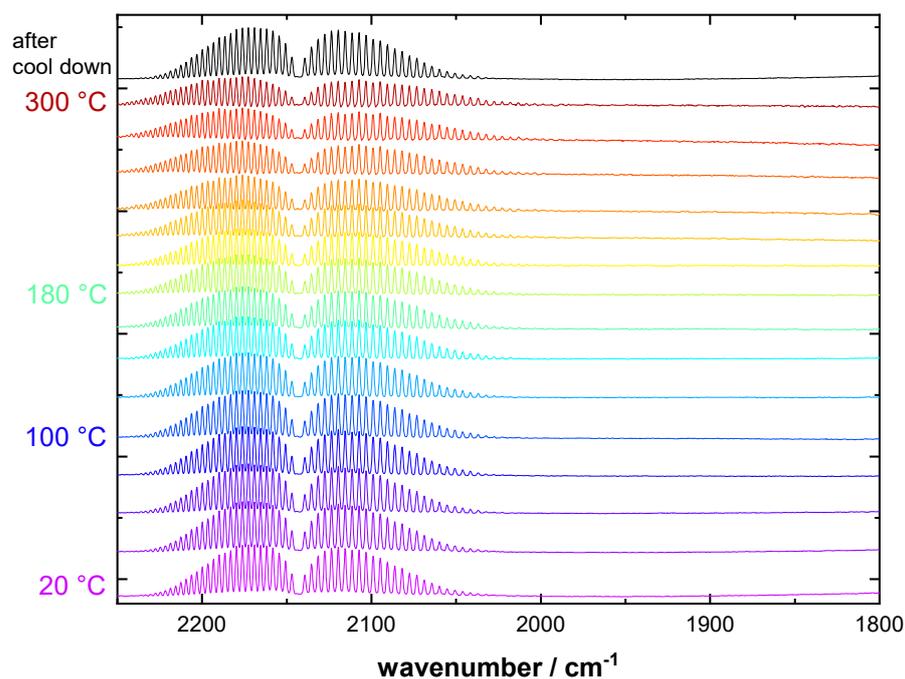
## XPS fit parameter and IrO<sub>2</sub>@TiO<sub>2</sub> reduction attempts

**Table S1.** XPS fit parameters.

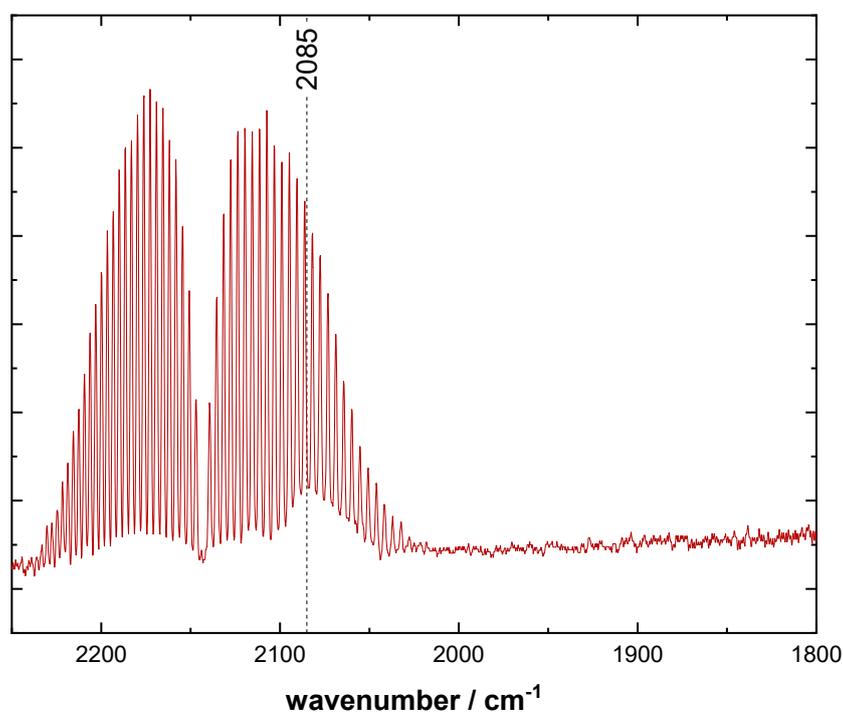
Species	Peak	Binding energy	FWHM	Fitting parameters
Ir	4f <sub>7/2</sub>	60.8	1.03	LF(0.6,1,150,300)
	4f <sub>5/2</sub>	63.8	1.03	LF(0.6,1,150,300)
IrO <sub>2</sub>	4f <sub>7/2</sub>	61.5	1.30	LF(0.3,1,65,300)
	4f <sub>5/2</sub>	64.5	1.47	LF(0.3,1,65,300)
TiO <sub>2</sub>	3s	61.9	3.04	GL(30)

The Ir<sup>0</sup> 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 TiO<sub>2</sub>, due to SMSI and/or form a mixed Ir-Ti oxide. We have however not investigated this further.

## Blank DRIFT Spectra of rutile-TiO<sub>2</sub> without active component



**Figure S7.** DRIFT spectra of pre-oxidized TiO<sub>2</sub> heated in a CO atmosphere. CO adsorption bands are not observed, while the RoVi fine structure of CO gas appears between 2100-2200 cm<sup>-1</sup>. 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<sup>-1</sup>.



**Figure S8.** DRIFTS spectrum of CO adsorption on Ir<sup>0+</sup>TiO<sub>2</sub> after oxidative pretreatment under 4% O<sub>2</sub> at 300°C for 12h. As previously shown for IrO<sub>2</sub>@TiO<sub>2</sub> only one band without broad shoulder is observed.