

Supporting information material to

An emission spectroscopy study of Pt/Al₂O₃ and

Pt/CeO₂/Al₂O₃

Valentina Marchionni,^{1,2} Jakub Szlachetko,^{1,3} Maarten Nachtegaal,¹ Anastasios Kambolis,¹ Oliver

Kröcher,^{1,4} Davide Ferri^{1*}

¹ Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

² ETH Zurich, Institute for Chemical and Bioengineering, CH-8093 Zurich, Switzerland

³ Jan Kochanowski University, Institute of Physics, PL-25-406 Kielce, Poland

⁴ École polytechnique fédérale de Lausanne (EPFL), Institute of Chemical Science and Engineering, CH-1015 Lausanne, Switzerland

* Corresponding author.

Phone: +41 56 310 27 81

e-mail: davide.ferri@psi.ch

Reference spectra for RXES

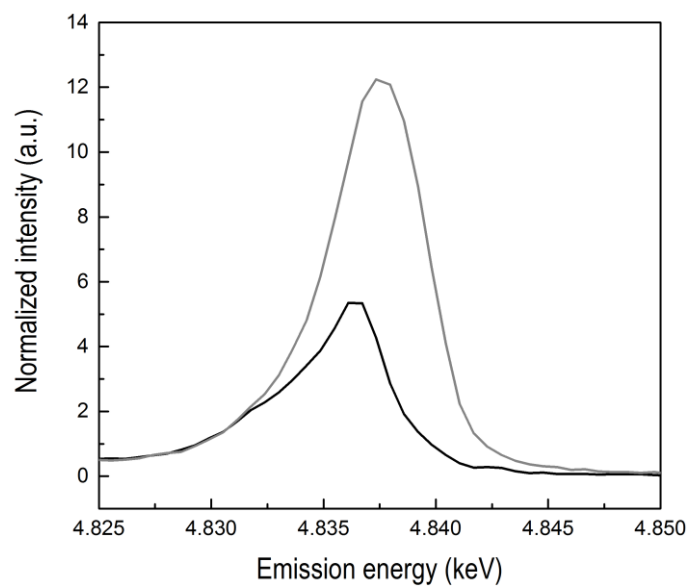


Figure S1. RXES spectra of calcined Pt/CeO₂/Al₂O₃ at room temperature in Ar (black, oxidized state) and after the H₂-TPR in 5 vol% H₂/Ar at 300°C (grey, reduced state).

Not normalized HEROS spectra collected during 1 vol% H₂ – 1 vol% O₂ modulation experiments

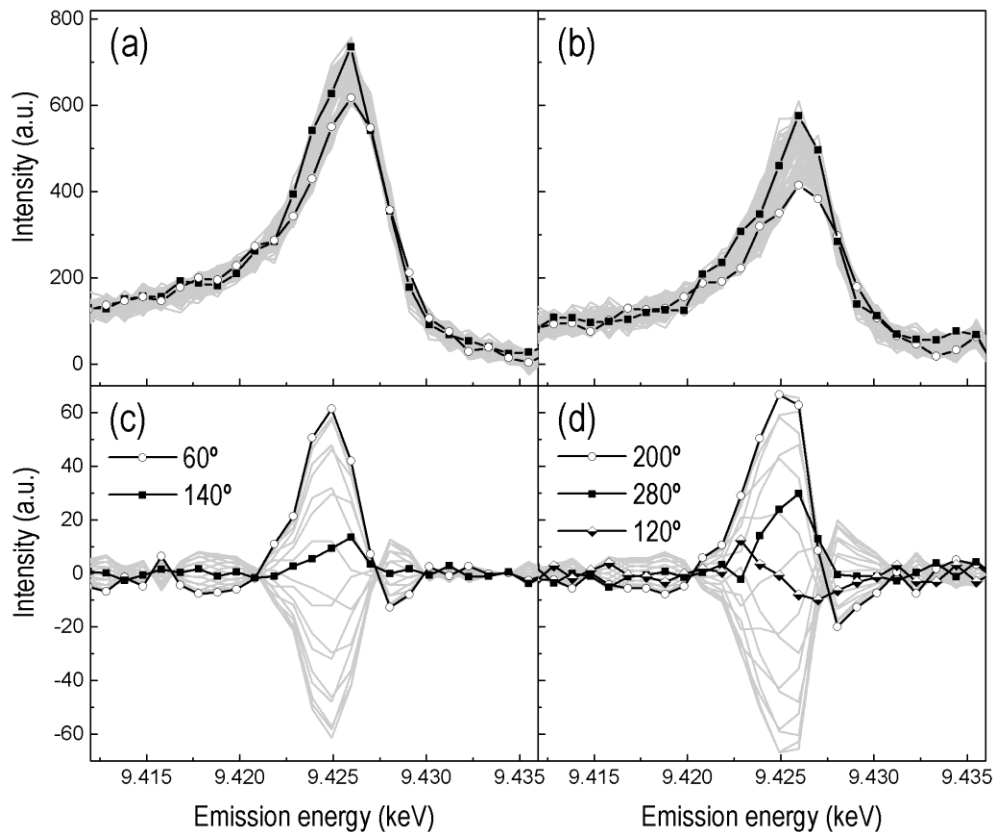


Figure S2. (a,b) Time-resolved and (c,d) phase-resolved HEROS spectra collected at the Pt L₃-edge during the 1 vol% H₂/He-1 vol% O₂/He modulation experiment (period 30+30 s, 120 cycles; 500 ms/spectrum) at 300°C on (a,c) Pt/Al₂O₃ and (b,d) Pt/CeO₂/Al₂O₃.

Comparison of 4 vol% H₂ – 4 vol% O₂ and 1 vol% H₂ – 1 vol% O₂ modulation experiments

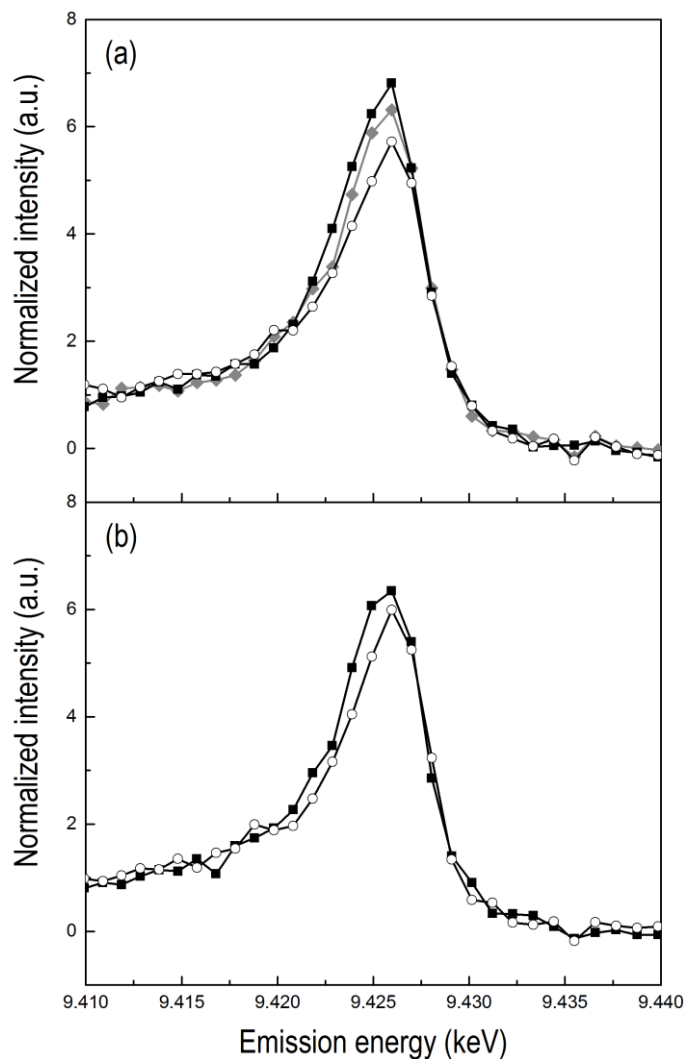


Figure S3. Selected time-resolved HEROS spectra collected during (a) 4 vol% H₂/He - 4 vol% O₂/He and (b) 1 vol% H₂/He - 1 vol% O₂/He modulation experiments on Pt/Al₂O₃ at 300°C. (○) Final reduced state, (◊) intermediate oxidized state and (■) final oxidized state.

Comparison of 4 vol% CO – 4 vol% O₂ and 1 vol% CO – 1 vol% O₂ modulation experiments

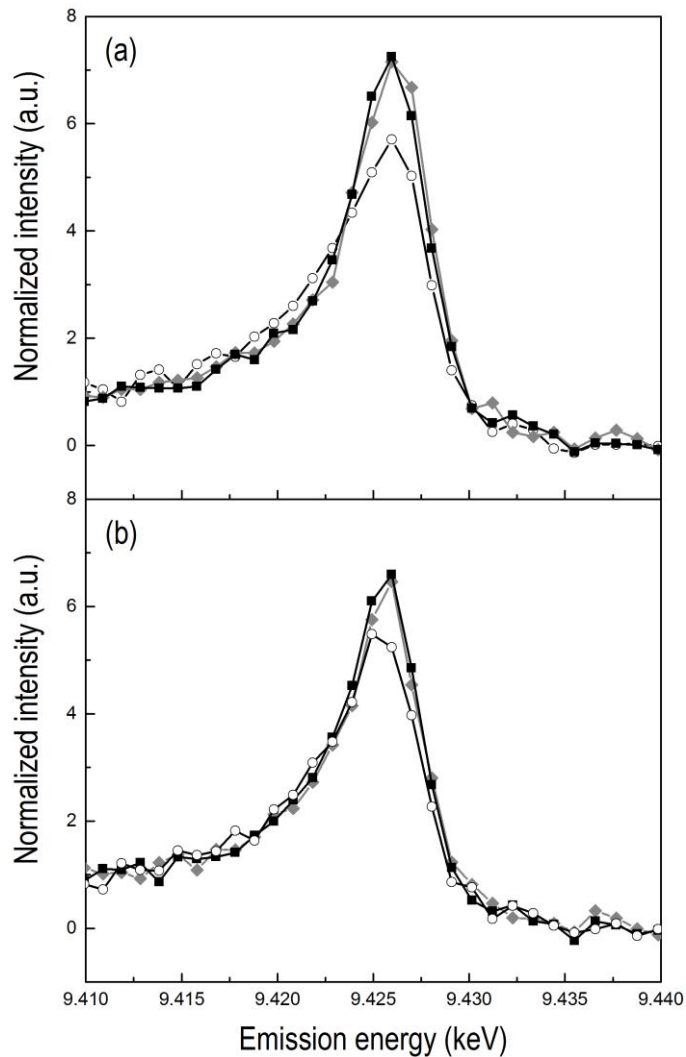


Figure S4. Selected time-resolved HEROS spectra collected during (a) 4 vol% CO/He - 4 vol% O₂/He and (b) 1 vol% CO/He - 1 vol% O₂/He modulation experiments on Pt/Al₂O₃ at 300°C. (○) Final reduced state, (◇) intermediate oxidized state and (■) final oxidized state.

DRIFTS CO-O₂ modulation experiment

The 1 vol% CO/He-1 vol% O₂/He modulation experiment was performed on Pt/Al₂O₃ at 300°C by collecting DRIFT spectra under identical experimental conditions to those discussed in the main manuscript. **Figure S1** shows that in the CO pulse CO adsorbs mainly as linearly bound CO on reduced Pt sites (2060 cm⁻¹). Simultaneously, a shoulder appears at 2077 cm⁻¹ that is due to linearly adsorbed CO on single Pt atoms with higher coordination degree. A third signal grows with some delay at 1999 cm⁻¹ that is attributed to linearly CO adsorption on poorly coordinated Pt atoms. A smaller fraction of twofold bridged coordinated CO is characterized by the broad band at 1782 cm⁻¹, which agrees well with the presence of Pt particles of 2-3 nm diameter (Figure 3a). During the subsequent oxidation pulse, the shoulder at 1999 cm⁻¹ is the first signal to disappear completely and no adsorbed CO is overserved at the end of the pulse.

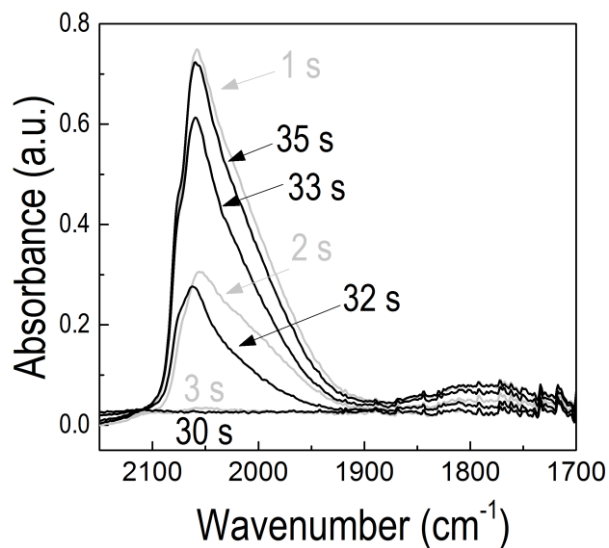


Figure S5. Selected averaged DRIFT spectra obtained in 1 vol% CO (black) and 1 vol% O₂ (grey) during the modulation experiment on Pt/Al₂O₃ at 300°C.