

Supplementary Information

Interplay between metal–support interaction and stability in Pt/Co₃O₄(111) model catalysts

Yaroslava Lykhach,^{a,*} Firas Faisal,^a Tomáš Skála,^b Armin Neitzel,^a Nataliya Tsud,^b Mykhailo Vorokhta,^b Filip Dvořák,^{b,†} Klára Beranová,^{b,‡} Yuliia Kosto,^b Kevin C. Prince,^c Vladimír Matolín,^b Jörg Libuda^{a,d}

^aLehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg,
Egerlandstrasse 3, 91058 Erlangen, Germany

^bCharles University, Faculty of Mathematics and Physics, Department of Surface and Plasma
Science, V Holešovičkách 2, 18000 Prague, Czech Republic

^cElettra-Sincrotrone Trieste SCpA, Strada Statale 14, km 163.5, 34149 Basovizza-Trieste, Italy

^dErlangen Catalysis Resource Center, Friedrich-Alexander-Universität Erlangen-Nürnberg,
Egerlandstrasse 3, 91058 Erlangen, Germany

yaroslava.lykhach@fau.de; Fax: +49 9131 8528867

* corresponding author

† present address: CEMNAT, Faculty of Chemistry and Technology, University of Pardubice, Nam. Cs. Legii 565,
53002 Pardubice, Czech Republic

‡ present address: Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 18221 Prague, Czech Republic

S1. Oxidation of Pt/Co₃O₄(111) model catalyst

Thermal stability of Pt/Co₃O₄(111) model catalyst upon annealing in oxygen atmosphere was investigated for Pt coverages of 0.6 and 1.1 ML. The following study supplements the findings discussed in Sections 3.2 and 3.3. The corresponding Pt 4f spectra and the development of the integrated intensities of the Pt 4f components are plotted as a function of temperature in Figure S1.

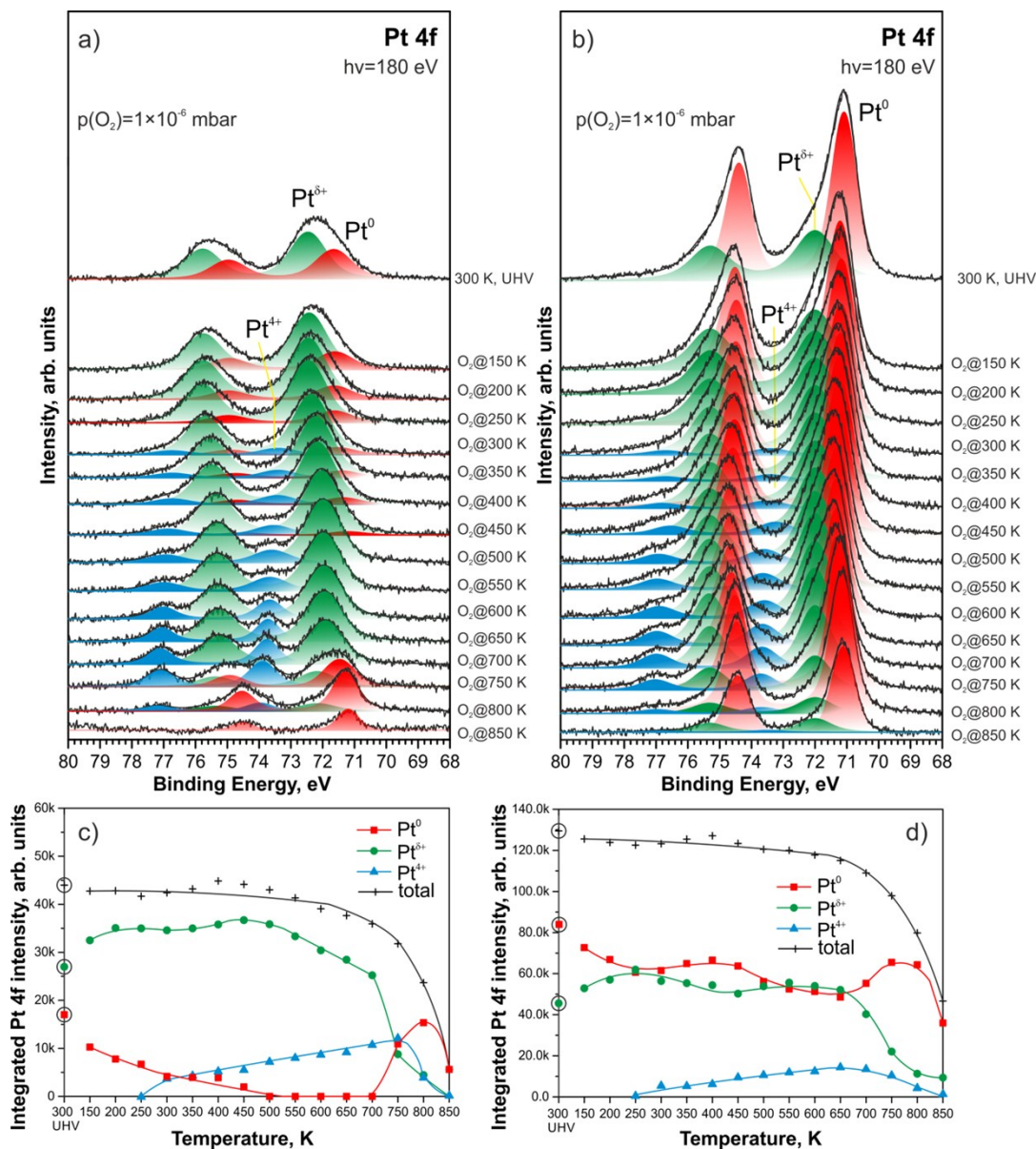


Figure S1. The evolution of Pt 4f spectra (a, b) and integrated Pt 4f intensities (c, d) for 0.6 ML (a, c) and 1.1 ML Pt/Co₃O₄(111) (b, d) as a function of temperature upon annealing in oxygen (1 × 10⁻⁶ mbar) for 3 min. The points marked with circles in c-d indicate the intensities of Pt 4f components prior to oxygen exposure. All spectra were acquired with photon energy of 180 eV.

The Pt 4f spectra obtained from as-prepared 0.6 and 1.1 ML Pt/Co₃O₄(111) model catalysts contain the contributions from both Pt^{δ+} and Pt⁰ species (see top traces in Figures S1a and S1b). We note that the nominal coverage of 0.6 ML Pt was used instead of 0.3 ML Pt (discussed in Section 3.3) in order to obtain similar Pt^{δ+}/Pt⁰ intensity ratio in the Pt 4f spectra (compare Figures S1 and 4a). These inconsistencies in the shapes of Pt 4f spectra are likely related to the differences in the crystallinity of the Co₃O₄(111) film or Pt deposition rate.

The exposure of the Pt/Co₃O₄(111) model catalyst to 1×10⁻⁶ mbar of O₂ resulted in the decrease of Pt⁰ and the increase of Pt^{δ+} signal at both Pt coverages, 0.6 and 1.1 ML. This observation is consistent with chemisorption of oxygen between 150 and 250 K.^{S1} At 300 K, the contributions from Pt⁴⁺ were detected in the Pt 4f spectra obtained from both 0.6 and 1.1 ML Pt/Co₃O₄(111). The Pt⁴⁺ intensities increase with temperature up to 750 K (0.6 ML) and 650 K (1.1 ML). As discussed in Section 3.2, the signal from Pt^{δ+} overlaps with the contribution from Pt²⁺ state which is associated with the formation of PtO. The PtO usually accompanies the formation of PtO₂.^{S1}

First, we discuss the differences observed upon annealing of 0.6 ML Pt/Co₃O₄(111) under UHV and in oxygen atmosphere. These are related to the formation of interfacial Pt oxide already at 300 K followed by complete oxidation of Pt particles between 500 and 700 K upon annealing in O₂ (Figure S1a). In particular, annealing of Pt/Co₃O₄(111) in oxygen atmosphere prevents reduction of Pt^{δ+} to Pt⁰ which was observed above 400 K upon annealing in UHV (compare Figures S1c and 4c). Note that above 600 K, metal–support interaction, which led to the formation of interfacial Pt oxide, most likely contributes to the oxidation of Pt particles also upon annealing in oxygen. Above 700 K, Pt⁰ signals increase at the expense of both Pt^{δ+} (and/or Pt²⁺) and Pt⁴⁺. Based on the development of the total integrated Pt 4f intensities we conclude that the stability of 0.3 ML and 0.6 ML Pt coverage annealed in UHV and in oxygen, respectively, is similar.

Next, we analyze the stability of 1.1 ML Pt/Co₃O₄(111) upon annealing in oxygen. In contrast to annealing of 1.3 ML Pt/Co₃O₄(111) in UHV, we observed formation of interfacial Pt oxide following the exposure to 1×10⁻⁶ mbar of O₂ at 300 K. In this respect, both 0.6 and 1.1 ML Pt/Co₃O₄(111) systems behave similarly. In contrast, the formation of interfacial Pt oxide at larger Pt coverage (1.93 ML, discussed in Section 3.2) was found to be kinetically hindered and occurs above 400 K under similar conditions (Figure 3b). Noteworthy, upon annealing in oxygen, the stability of supported Pt particles is similar for all investigated Pt coverages, i.e. 0.6, 1.1, and 1.93 ML. This observation suggests that Pt particles can be stabilized at large Pt coverages under oxidizing conditions due to the formation of interfacial Pt oxide.

References

S1. Miller, D. J.; Öberg, H.; Kaya, S.; Sanchez Casalongue, H.; Friebel, D.; Anniyev, T.; Ogasawara, H.; Bluhm, H.; Pettersson, L. G. M.; Nilsson, A., Oxidation of Pt(111) under Near-Ambient Conditions. *Phys. Rev. Lett.* **2011**, *107*, 195502.