Supplementary Information

Interplay between metal–support interaction and stability in Pt/Co$_3$O$_4$(111) model catalysts

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S1. Oxidation of Pt/Co$_3$O$_4$(111) model catalyst

Thermal stability of Pt/Co$_3$O$_4$(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/Co$_3$O$_4$(111) (b, d) as a function of temperature upon annealing in oxygen ($1 \times 10^{-6}$ 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/Co$_3$O$_4$(111) model catalysts contain the contributions from both Pt$^{\delta^+}$ and Pt$^0$ 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$^{\delta^+}$/Pt$^0$ 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 Co$_3$O$_4$(111) film or Pt deposition rate.

The exposure of the Pt/Co$_3$O$_4$(111) model catalyst to $1 \times 10^{-6}$ mbar of O$_2$ resulted in the decrease of Pt$^0$ and the increase of Pt$^{\delta^+}$ signal at both Pt coverages, 0.6 and 1.1 ML. This observation is consistent with chemisorption of oxygen between 150 and 250 K. At 300 K, the contributions from Pt$^{\delta^+}$ were detected in the Pt 4f spectra obtained from both 0.6 and 1.1 ML Pt/Co$_3$O$_4$(111). The Pt$^{\delta^+}$ 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$^{\delta^+}$ overlaps with the contribution from Pt$^{2+}$ state which is associated with the formation of PtO. The PtO usually accompanies the formation of PtO$_2$. First, we discuss the differences observed upon annealing of 0.6 ML Pt/Co$_3$O$_4$(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 O$_2$ (Figure S1a). In particular, annealing of Pt/Co$_3$O$_4$(111) in oxygen atmosphere prevents reduction of Pt$^{\delta^+}$ to Pt$^0$ 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, Pt$^0$ signals increase at the expense of both Pt$^{\delta^+}$ (and/or Pt$^{2+}$) and Pt$^{4+}$. 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/Co$_3$O$_4$(111) upon annealing in oxygen. In contrast to annealing of 1.3 ML Pt/Co$_3$O$_4$(111) in UHV, we observed formation of interfacial Pt oxide following the exposure to $1 \times 10^{-6}$ mbar of O$_2$ at 300 K. In this respect, both 0.6 and 1.1 ML Pt/Co$_3$O$_4$(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