Supporting Information

Effect of the Ru concentration on the CO tolerance and the oxidizability of a composition spread PtRu/Pt(111) near-surface alloy

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Characterization of the Ru wedge

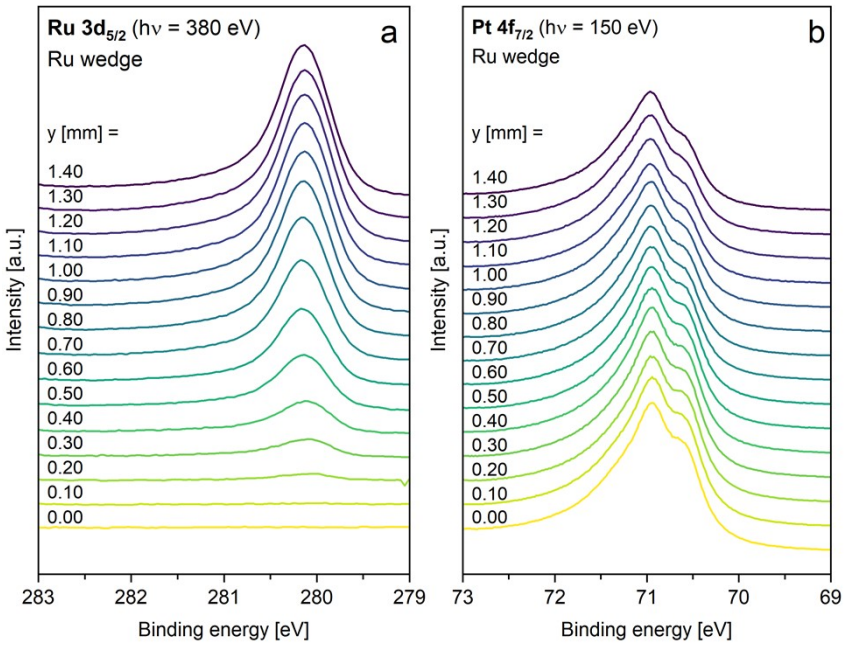

Figure S1. Ru $3d_{5/2}$/Pt $4f_{7/2}$ y scan (a/b) after deposition of the wedge-shaped Ru gradient and subsequent flash-annealing to 600 K.

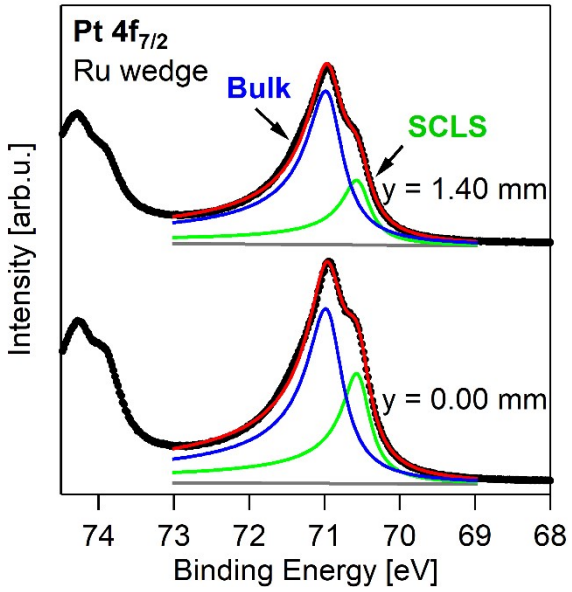

Figure S2. Selected spectra from the Pt 4f y scan after deposition of the wedge-shaped Ru gradient and subsequent flash-annealing to 600 K including the applied fit model; (y = 0.00 mm) Ru-free, pristine Pt(111); (y = 1.40 mm) position of maximal Ru 3d signal intensity.

Table S1. Fit parameters applied in the quantitative analysis of the Pt 4f y scan after deposition of the wedge-shaped Ru gradient and subsequent flash-annealing to 600 K (shown above).

Contribution	Binding Energy [eV]	Gaussian Width [eV]	Lorentzian Width [eV]	Asymmetry Factor
Pt $4f_{7/2}$ SCLS	70.54	0.06	0.19	0.22
Pt $4f_{7/2}$ Bulk	70.94	0.06	0.24	0.22

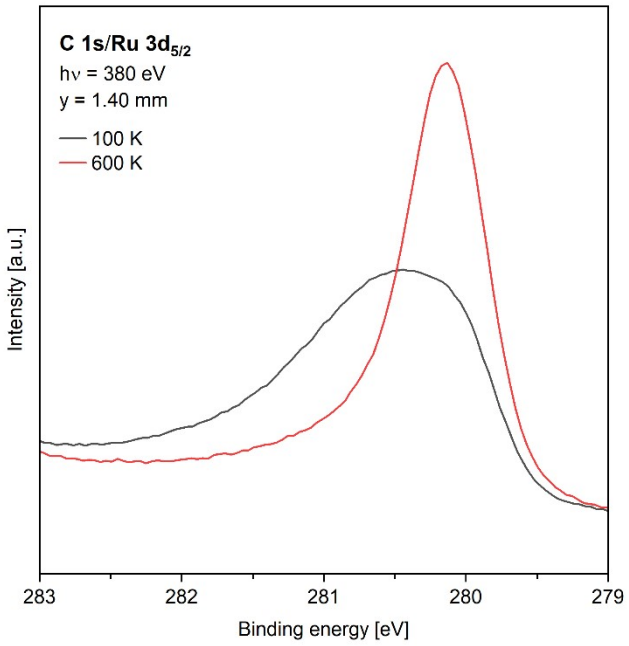

Figure S3. Comparison of the Ru $3d_{5/2}$ spectra recorded after Ru deposition at 100 K (black) and subsequent flash-annealing to 600 K (red) at the position y = 1.40 mm.

Determination of the Ru coverage

The local Ru coverage, θ_{Ru}, at the apex of the 600 K annealed wedge (y = 1.40 mm) was determined based on the following considerations:

For a uniform film of θ_{Ru} = 1 ML (monolayer) on the Pt(111) substrate, the attenuation of the Pt $4f_{7/2}$ signal is calculated according to the equation:

$$\frac{I_d}{I_0} = e^{-d/\lambda \times \cos\vartheta}$$

I_d and I_0 are the Pt $4f_{7/2}$ intensities of the Ru-covered and the pristine Pt substrate, respectively. d is the thickness of the 1 ML Ru film, that is, 2.15 Å according to the interlayer spacing in Ru(0001). λ is the inelastic mean free path (IMFP) of the Pt $4f_{7/2}$ electrons in Ru, that is, 4.17 Å according to the TPP2M algorithm[1] (at E_{kin} ~79 eV, for E_B ~71 eV with $h\nu$ = 150 eV), and ϑ is the emission angle with respect to the surface normal, that is, 0° (normal emission) in our measurements. Inserting these values yields an attenuation for a 1 ML thick Ru film of: $\frac{I_d}{I_0} \approx 0.597$

For θ_{Ru} <1 ML, we expect a linear behavior with the condition that the linear equation intercepts the exponential curve at θ_{Ru} = 1 ML (this is graphically illustrated in Figure S3).

$$\frac{I_d}{I_0} = 1 - m \times \theta$$

With $m \approx 0.403$ and $\frac{I_d}{I_0} \approx 0.775$, we obtain a Ru coverage of $\theta_{Ru} \approx 0.559\ ML$ for the wedge at the position of maximal Ru 3d signal intensity, y = 1.40 mm. The Ru coverages at the other y positions of the wedge and after flash-annealing the wedge to 850 K (PtRu near-surface alloy) were determined by referencing the respective Ru $3d_{5/2}$ signal to the Ru $3d_{5/2}$ signal of the wedge at y = 1.40 mm (θ_{Ru} = 0.559 ML).

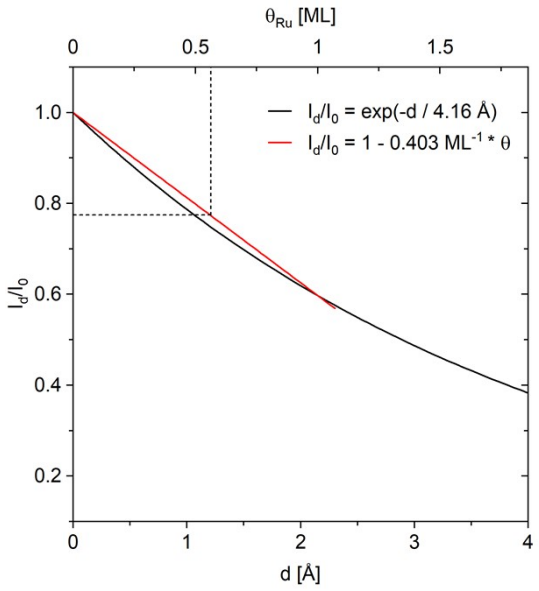

Figure S4. Graphical illustration of the linear equation used to calculate the Ru coverage of the 600 K annealed wedge at y = 1.40 mm.

The observed damping of the Pt $4f_{7/2}$ SCLS $\frac{I_d}{I_0} = 0.586$ suggests that only 0.414 ML of the surface Pt atoms are covered by Ru. We attribute this deviation to some of the Ru in the non-alloyed wedge being present in the form of 3-dimensional (bilayer) islands and/or in the first subsurface layer. Assuming that the difference in both coverages $0.559\ ML - 0.414\ ML$ is due to Ru in bilayer islands, the coverage can be corrected by multiplying this difference by a factor of $\frac{0.596}{0.355}$, that is, $\frac{I_d\,(for\ 1\ ML\ Ru)}{I_d\,(for\ 2\ ML\ Ru)}$. This way, a maximum Ru coverage of $0.414\ ML + 0.243\ ML = 0.657\ ML$ (at y = 1.40 mm) is obtained. Thus, we assume that the calculated coverage of 0.56 ML underestimates the actual Ru coverage by at most 0.10 ML. Notably, this value matches well to the observed attenuation of the Ru 3d signal after flash-annealing the wedge to 850 K under the assumption that all of the Ru in the PtRu near-surface alloy has moved to the 2nd layer. In this scenario, the Ru signal would be damped by one monolayer of Pt according to:

$$\frac{I_d}{I_0} = e^{-d/\lambda \times \cos\vartheta}$$

With λ = 3.81 Å[1] and d = 2.226 Å[2], a value of $\frac{I_d}{I_0} \approx 0.557$ is obtained. Multiplying this factor by the corrected coverage of 0.657 ML yields an apparent coverage of the alloyed wedge of θ_{Ru} = 0.37 ML, which matches well to the observed 0.40 ML in our experiment (see Figure 2 of the main manuscript).

Adsorption of CO

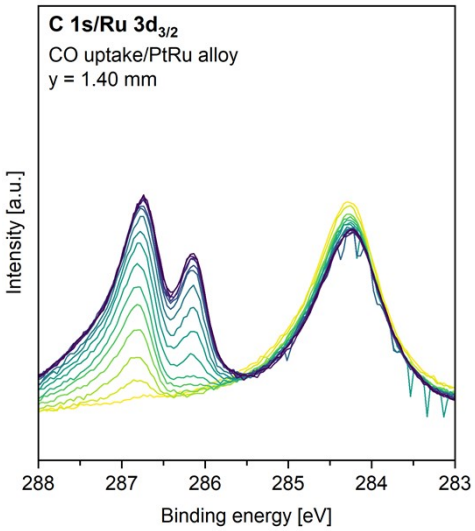

Figure S5. Exposure of the PtRu near-surface alloy to CO until saturation (10.7 L). The spectra were measured in situ at the position of maximal Ru concentration, y = 1.40 mm.

CO TPXPS

As a final step of our study on the adsorption of CO on the PtRu near-surface alloy, CO was removed again from the sample in a temperature-programmed XPS experiment. That is, after recording the y scan depicted in Figure 3 of the manuscript, the sample was heated linearly at 0.5 K s^{-1} using a bifilar coil filament located at the back of the crystal, and the desorption of CO was followed *in situ* by XPS in the C 1s region at the position of maximum Ru concentration, y = 1.40 mm. The acquired spectra are shown as waterfall plot in Figure S6a. For comparison, we also provide data from a previous TPXPS experiment of CO on bare Pt(111) on the right, see Figure S6c. The experiments were fitted with the same parameters as detailed in the main manuscript and the resulting quantitative plots are presented in the bottom (Figure S6c). The desorption temperatures can be estimated from the inflection points of the curves, which are indicated by the green arrows. The analysis shows a CO desorption temperature for the PtRu near-surface alloy of about 345 K. This value is around 35 K lower than that observed for the bare Pt(111) reference, that is, 380 K. The results can be interpreted as a weaker adsorption energy of CO on the PtRu near-surface alloy as compared to CO adsorption on Pt(111), which is in excellent agreement with the results of earlier reports on PtRu/Ru(0001) alloys and Pt monolayer film covered Ru(0001) surfaces.[3-5]

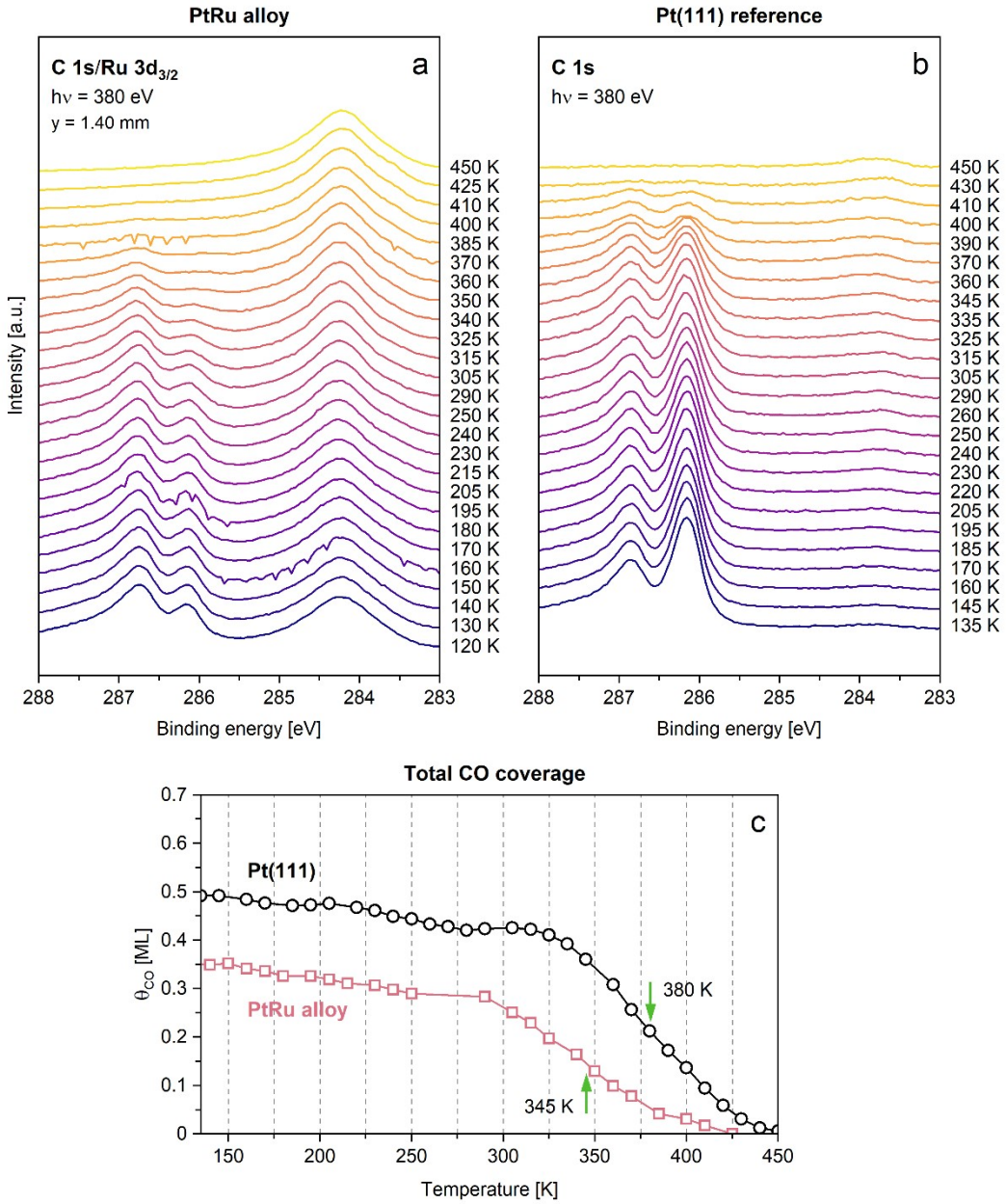

Figure S6. a) C 1s TPXPS of CO on the PtRu near-surface alloy recorded at the position y = 1.40 mm just after the y scan shown in Figure 3 of the manuscript. b) C 1s TPXPS of 0.5 ML CO on Pt(111) for reference. c) Comparison of the total CO coverages as a function of temperature. The green arrows mark the inflection points of both curves, which were used to estimate the desorption temperatures.

Table S2. Fit parameters applied in the quantitative analysis of the Ru 3d/C 1s y scan of the as-prepared PtRu near-surface alloy. See manuscript, Figure 2c.

Contribution	Binding Energy [eV]	Gaussian Width [eV]	Lorentzian Width [eV]	Asymmetry Factor
Ru $3d_{5/2}$	280.05	0.32	0.14	0.20
Ru $3d_{3/2}$	284.23	0.32	0.34	0.20
Carbide	284.0	0.75	0.08	0.07

Table S3. Fit parameters applied in the quantitative analysis of the CO covered PtRu near-surface alloy. See manuscript, Figure 3b.

Contribution	Binding Energy [eV]	Gaussian Width [eV]	Lorentzian Width [eV]	Asymmetry Factor
Ru $3d_{5/2}$	280.03	0.32	0.14	0.20
Ru $3d_{3/2}$	284.21	0.32	0.34	0.20
Carbide	284.0	0.75	0.08	0.07
$CO^{Pt,\ bridge}$	286.10	0.21	0.12	0.14
$CO^{Pt,\ on\text{-}top}$	286.69 (+0.08)	0.21	0.13	0.37

Table S4. Fit parameters applied in the quantitative analysis of the PtRu near-surface alloy after exposure to O_2 at 600 K. See manuscript, Figure 4b.

Contribution	Binding Energy [eV]	Gaussian Width [eV]	Lorentzian Width [eV]	Asymmetry Factor
Ru $3d_{5/2}$	280.05	0.32	0.14	0.20
Ru $3d_{3/2}$	284.23	0.32	0.34	0.20
RuO_x $3d_{5/2}$	280.62	0.32	0.14	0.20
RuO_x $3d_{3/2}$	284.80	0.32	0.41	0.20
Carbide	284.3	0.75	0.08	0.07

References

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