The 2nd Order Dependence on the Surface Fraction of Pt in Pt-Ru$_{adatom}$ of the Oxidation of 2-PrOH in Base

Supporting

1   XPS of PtRu$_{Xad}$

Figure S**1** shows the high-resolution XPS spectra of Pt$_{Black}$ and the PtRu$_{Xad}$ catalysts in the BE region for Ru 3d electrons. Two peaks from carbon 1s are also present in this BE region. Upon addition of Ru four new Ru 3d$_{5/2}$ peaks are observed at 280.3, 280.9, 281.9, and 282.9 eV. These peaks are assigned to Ru^0, RuO$_2$, RuCl$_3$, and RuO$_3$, respectively, and are in agreements with the reports by Kim et al. [1] and Folkesso[2]. Note that the intensity scale for each catalyst differs, and scales are chosen to maximize the viewable area.
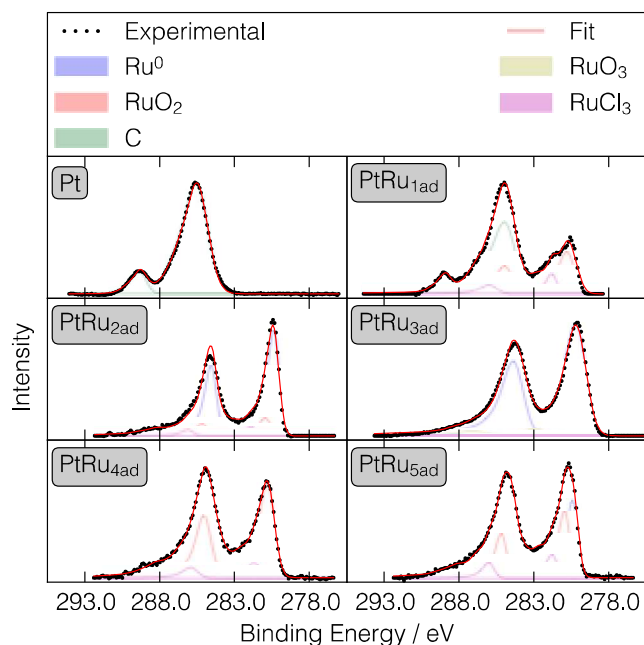

Figure S1 - High-resolution XPS spectra of the Pt$_{Black}$ and PtRu adatom catalysts in the BE region for Ru 3d electrons. Colored curves show the results of the component fitting analysis

Figure S**2** shows the high-resolution XPS spectra in the Pt BE region for the same catalysts shown in Figure S**1**. Pt $4f_{7/2}$ peaks are observed at 71.2 and 72.6 eV, and have been assigned to Pt^0 and $Pt(OH)_2$, respectively. These assignments agree well with values reported by Hammond and Winograd.[3].
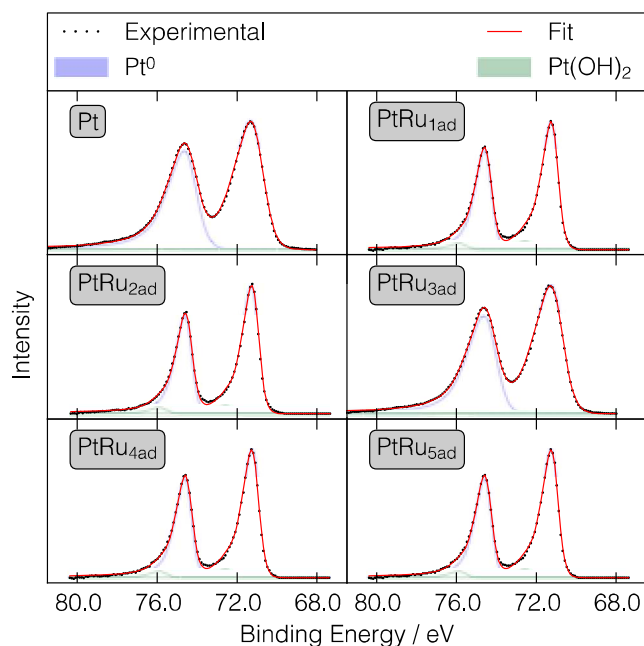

Figure S2 - High-resolution XPS spectra of the Pt$_{Black}$ and PtRu$_{Xad}$ catalysts in the BE region for Pt 4f electrons. Colored curves show the results of the component fitting analysis

Figure S**3** plots the A_{ms} of Pt versus the A_{ms} of Ru for the six catalysts prepared for this study. A linear trend is observed with a slope of -1.2 ± 0.1. A slope = -1 would imply a 1:1 coverage of surface Pt by surface Ru. Significant amounts of Ru deposition on Ru would increase the Ru area while not changing the Pt area, resulting in a slope < -1. We therefor interpret this as an indication that the Ru is predominantly deposited in a 2D layer on Pt. This analysis gives no information, however, on the dispersion of the Ru sites, or if the 2D nature of the Ru deposit forms during the deposition itself or if it is a result of surface reorganization during annealing or conditioning. We regard the PtRu$_{Xad}$ catalysts used in this as mostly 2D sublayers of Ru on a bulk Pt surface.
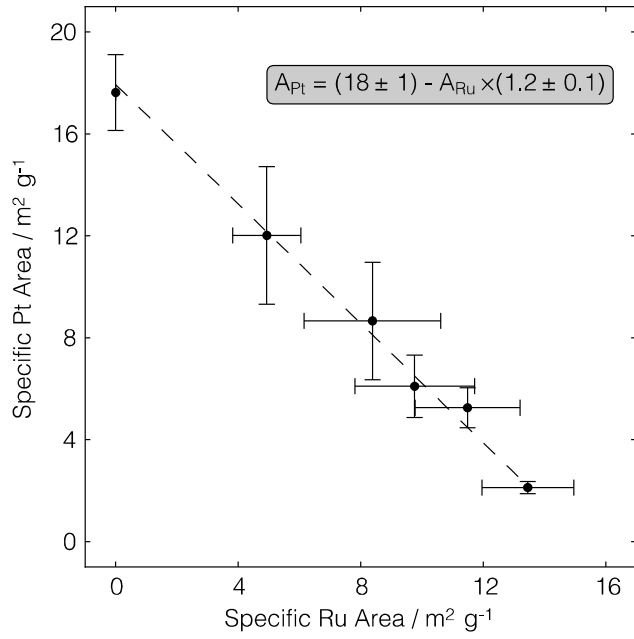
Figure S3 - Plot of the mass-specific surface area of Pt as a function of the mass-specific surface area of Ru in the PtRu$_{Xad}$ catalysts.

2 *Deconvolution of kinetic and thermodynamic parameters*

The proposal that $k_{apparent}$ can be expressed in terms of parallel pathways on Pt and on Ru requires that $\Delta H^{\ddagger}_{apparent}$ and $A_{apparent}e^{\Delta S^{\ddagger}(apparent)/R}$ can also be expressed by an activation enthalpy and entropy terms for each pathway. The values of $\Delta H^{\ddagger}_{Pt}$, $\Delta H^{\ddagger}_{Ru}$, $A_{Pt}e^{\Delta S^{\ddagger}(Pt)/R}$, and $A_{Ru}e^{\Delta S^{\ddagger}(Ru)/R}$ were evaluated numerically from

$$k_{apparent}=k_{Pt}\theta_{Pt}^2 + k_{Ru}(1-\theta_{Pt}) \qquad \text{Eq. 1}$$

$$\Delta H^{\ddagger}_{apparent,\theta}= \frac{\delta ln(k_{apparent,\theta})}{\delta T} \times R \qquad \text{Eq. 2}$$

and

$$A_{apparent,\theta}e^{\Delta S^{\ddagger}_{apparent,\theta}}= lim_{T\to\infty} (k_{apparent,\theta}) \qquad \text{Eq. 3}$$

Figure S**4** plots the resulting fits for of $k_{apparent}$, $\Delta H^{\ddagger}_{apparent}$, and $A_{apparent}e^{\Delta S^{\ddagger}(apparent)/R}$ as a function of θ_{Ru}, and also reports the fitted values of $\Delta H^{\ddagger}$ and $Ae^{\Delta S^{\ddagger}/R}$ for Pt and Ru. Note that all three experimental variables were fitted simultaneously. Pt$_{Black}$ is not included in the fitting, but rather used as a validation set.
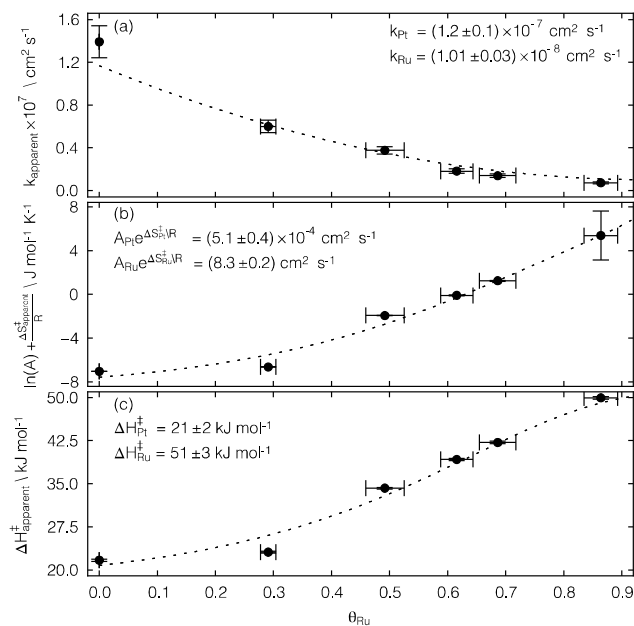
Figure S4 - Plots of the fitted (a) $k_{apparent}$, (b) $A_{apparent}e^{\Delta S^{\ddagger}(apparent)/R}$, and (c) $\Delta H^{\ddagger}_{apparent}$ for the PtRu$_{Xad}$ catalyzed oxidation of 2-propanol in alkaline electrolytes at E^0. The enthalpy and entropy terms for each component are also supplied in the plot. Note that Pt$_{Black}$ was not included in the fitting, and was used as a test point to validate the model.

Reference

(1)   Kim, H.; de Moraes, R.; Tremiliosi-Filho, G.; Haasch, R.; Wieckowski, A. Chemical State of Ruthenium Submonolayers on a Pt(111) Electrode. *Surf Sci*., **2001**, *474*, L203–L212.

(2)   Folkesso, B. Esca Studies on Charge-Distribution in Some Dinitrogen Complexes of Rhenium, Iridium, Ruthenium, and Osmium. *Acta Chem Scand*. **1973**, *27*, 287–302.

(3)   Hammond, J. S.; Winograd, N. XPS Spectroscopic Study of Potentiostatic and Galvanostatic Oxidation of Pt Electrodes in H2SO4 and HClO4. *J Electroanal Chem*. **1977**, *78*, 55–69.