

## Reaction driven ordering of the surface of a PtRh alloy model catalyst

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During an X-ray diffraction study of CO oxidation over a Pt<sub>25</sub>Rh<sub>75</sub>(100) single crystal, an unexpected c(2 × 2) structure emerged, indicating that not only the adsorbate is important, but also the near-surface layers.

It has been shown that platinum group metals, such as Pt and Rh, are efficient oxidation catalysts [1, 2]. These two metals can with advantage be combined in a bimetallic alloy to improve the catalytic activity and selectivity, thermal stability, and make it more poison resistant compared to the pure metals [3]. Previous studies on PtRh(100) single crystals have shown that mildly oxidizing conditions cause a p(3 × 1) reconstruction with chemisorbed O to form [1, 4–8], while strongly oxidizing conditions entail a c(8 × 2) surface oxide [1, 4, 9]. Despite being well-studied, the PtRh system is not fully understood.

To gain a better understanding of this alloy system, we have studied CO oxidation over a Pt<sub>25</sub>Rh<sub>75</sub>(100) single crystal using high-energy surface X-ray diffraction (HESXRD) under reaction conditions. The study was performed at the beamline P21.2 at PETRA III, DESY, in Hamburg, Germany. Under oxidizing conditions, we found the two Rh–O structures mentioned in the previous paragraph. However, under reducing conditions and elevated temperature, we found an unexpected c(2 × 2) structure, see Figure 1a where the superstructure rods are indicated with white rings. This structure remained even when changing to more oxidizing conditions (up to CO:O<sub>2</sub> = 5 : 40).

CO adsorbs in a c(2 × 2) pattern on both Pt(100) [10] and Rh(100) [11], and thus we expect CO to adsorb in a c(2 × 2) pattern on Pt<sub>25</sub>Rh<sub>75</sub>(100). However, our analysis indicates that not only the adsorbate is contributing to the c(2 × 2) structure, but also the metal atoms in the surface or near-surface layers. There are undulations along the superstructure rods, as seen in Figure 1b, suggesting that more than one layer contributes to the c(2 × 2) structure. The first peak appears at  $q_{\perp} \approx 1 \text{ \AA}^{-1}$ , which corresponds to a maximum out-of-plane distance of atoms contributing to the c(2 × 2) structure of  $\frac{2\pi}{1 \text{ \AA}^{-1}} \approx 6 \text{ \AA}$ . This would approximately correspond to the distance between the O atom of the adsorbed CO and the third metal layer, as illustrated in Figure 1c.

The ongoing quantitative analysis, together with DFT calculations, however, suggests that the structure is more complex than this. In this presentation we will provide an update of the current status of the analysis and interpretation.

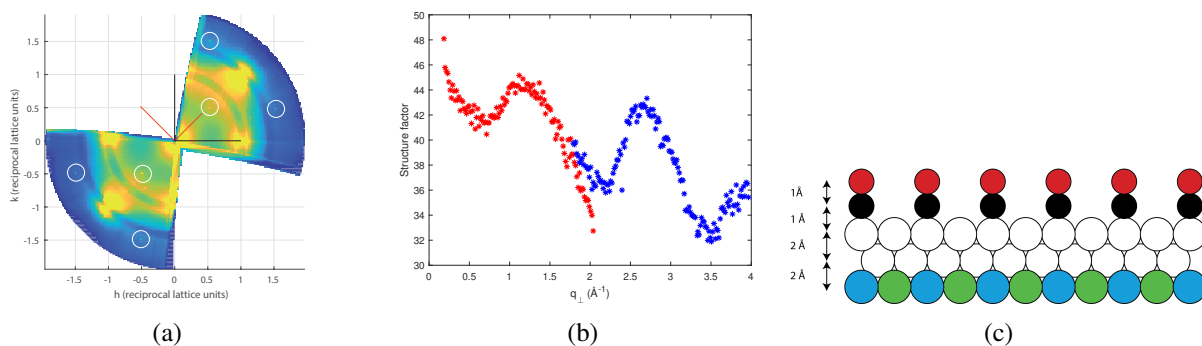


FIG. 1: (a) The HESXRD intensity shown as a projection in the  $h$ - $k$  plane. The  $c(2 \times 2)$  structure is revealed by the reflections marked with white rings. The black and red lines in the center of the plot mark the  $(1 \times 1)$  substrate unit cell and the  $c(2 \times 2)$  unit cell, respectively. (b) The structure factor as a function of  $q_{\perp}$  value for the  $(0.5, 0.5)$  (blue) and  $(0.5, 1.5)$  (red) rods. (c) Side view of the first three metal layers and the adsorbed CO.

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