

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

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Transition metals have proved to be efficient in oxidation catalysis [1, 2]. If two transition metals are combined in a supported bimetallic catalyst, this alloy catalyst may exhibit improved activity, selectivity, stability etc compared to the pure metals [3]. One bimetallic catalyst that is often used as a three-way catalyst in automobile engines for oxidation of CO and reduction of NO_x contains Pt and Rh [2–6]. There is a synergism between Pt and Rh in the bimetallic catalyst; for CO oxidation, Pt is more active than Rh during strongly oxidizing conditions, while the opposite is valid for reducing conditions [3]. The PtRh alloy system is well-studied, but not completely understood.

To better understand the catalytic reactions on the atomic level for this bimetallic catalyst, we investigated a Pt₂₅Rh₇₅(100) single-crystal using high-energy surface X-ray diffraction (HESXRD) at beamline P21.2 at PETRA III, DESY, in Hamburg, Germany. Under oxidizing conditions, we found two Rh-O structures that have been observed previously, namely a p(3×1) reconstruction with chemisorbed O [1, 4, 5] and a c(8×2) surface oxide [1, 5, 7]. Under reducing conditions, we found an unexpected c(2×2) structure, see Figure 1a. On Rh(100), CO adsorbs in this structure [1, 8], but the scattering from the adsorbate molecules is usually too weak to be observed in HESXRD. This indicates that we have an ordered surface of the substrate rather than only an adsorbate structure.

We drew the conclusions that the Pt and Rh atoms segregated during catalysis and formed an ordered surface alloy. Our suggested model was that CO molecules adsorb in a c(2×2) structure. The more reactive Rh atoms are pulled towards the adsorbed CO molecules while the Pt atoms are pulled towards positions without adsorbates. If this hypothesis was correct, it would be possible to create this ordered alloy by exposing the crystal to a suitable pressure of pure CO. Despite covering a CO pressure range of 10⁻⁷ mbar to 10⁻¹ mbar, we were not able to recreate the structure in this way. However, after this experiment, we annealed the sample in ultra-high vacuum (UHV), after which the c(2×2) was found. The updated hypothesis is that the gas exposure resulted in a first layer of Rh and a second layer of Pt. When annealing in UHV, the Pt atoms approached the surface, causing a mixed surface layer of 50 at% Pt and 50 at% Rh in a well-ordered c(2×2) structure, as shown in Figure 1b-c.

We see this as a new route to create systems similar to so-called single atom alloy catalysts, avoiding evaporation that is often very time consuming, especially during beamtimes. Further experiments including other alloys, such as Pd₃Au(100), are planned and will be carried out in the near future.

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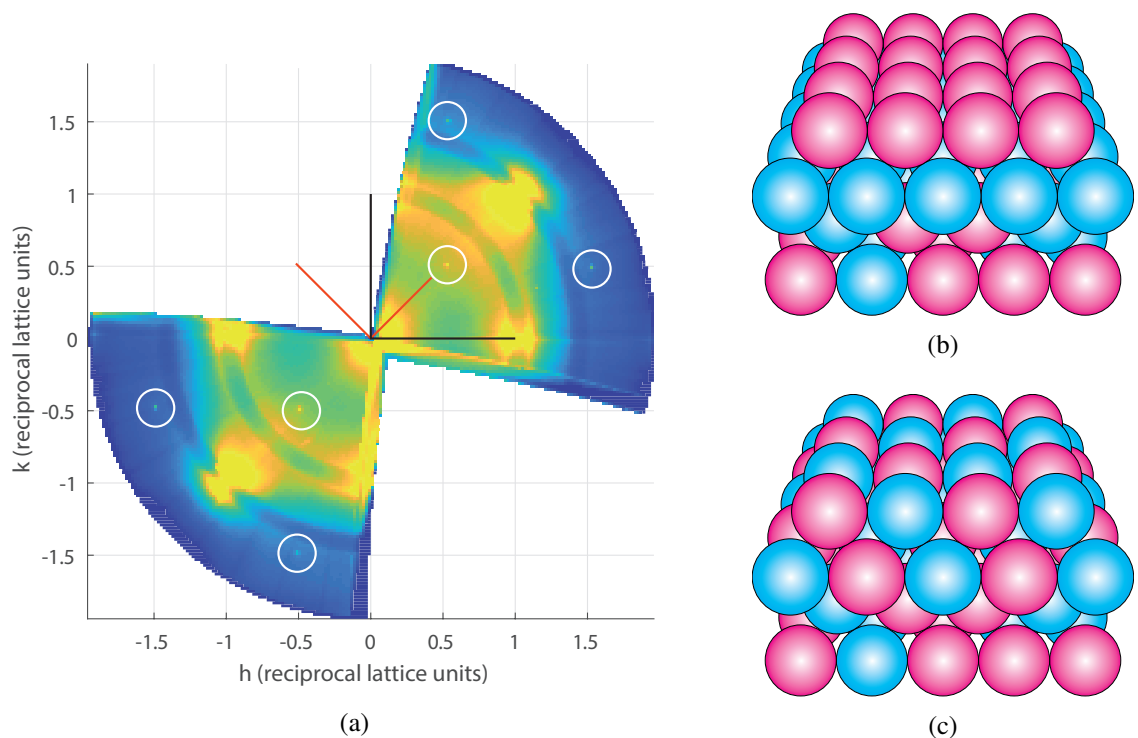


FIG. 1: a) An HESXRD plot of $\text{Pt}_{25}\text{Rh}_{75}(100)$ during reducing conditions and high temperature reveals the additional spots from the $c(2 \times 2)$ structure, marked by white rings. The black and red lines in the center of the plot mark the unit cells of $p(2 \times 2)$ and $c(2 \times 2)$, respectively. b) Gas exposure pulls out Rh atoms (magenta) to the surface, causing a second layer of Pt atoms (cyan). c) During annealing, Pt atoms segregate towards the surface and a mixed layer is formed, resulting in a well-ordered $c(2 \times 2)$ structure.

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