

## Multilayer Relaxation of Ru Studied by Surface X-ray Diffraction

The structure and composition of solid surfaces affect the chemical reactivity of heterogeneous catalysts. The elucidation of the structure of oxygen on metal surfaces is important for understanding electrochemical phenomena such as corrosion, oxidation, and oxygen reduction. In particular, adsorbed oxygen or hydroxyl groups on Ru surfaces play an important role in electrocatalysis of the oxidation of carbon monoxide (CO) by Pt/Ru catalysts in the direct methanol fuel cell (DMFC). The platinum surface is poisoned by CO formed during methanol oxidation. ( $\text{CH}_3\text{OH} \rightarrow \text{CO}_{\text{ad}} + 4\text{H}^+ + 4\text{e}^-$ ) Adsorbed CO is easily oxidized to  $\text{CO}_2$  by adsorbed oxygen atoms on the Ru surface (Fig. 1).

Surface relaxation influences electronic states, work functions, surface energy, and catalytic reactivity significantly. Detailed understanding of the structure of deeper layers is required to provide a realistic description of the surface electron structure. It is well-known that low-energy electron diffraction (LEED) is an excellent technique for determining the atomic arrangement on the metal surface. However, LEED measurement cannot precisely detect relaxation below the surface because low-energy electrons do not penetrate deep into a material. Surface X-ray diffraction is a powerful tool for investigating the

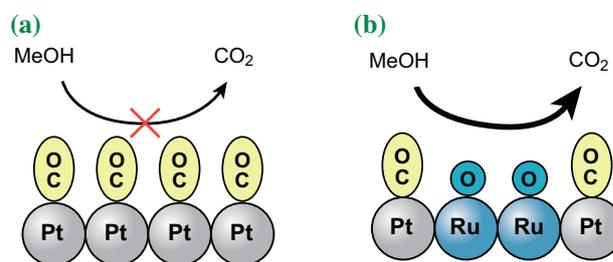


Fig. 1: Schematic model of methanol oxidation on (a) Pt and (b) Pt/Ru.

relaxation of subsurface areas as well as the reconstruction of the topmost layer. The structure of a Ru(001) surface after adsorbed-oxygen-induced surface relaxation was determined by surface X-ray diffraction using the UHV chamber on the (2 + 2) diffractometer at beamline **BL13XU**.

Oxygen is absorbed on the Ru(001) surface at hollow sites and forms an ordered (2 × 2) structure. Figure 2 shows the structure factors of diffraction rods at (0 0.5), (0.5 0), (0 1), and (1 0). Bragg peaks appear at integers  $L$  for the (1 0) and (0 1) crystal truncation rods (CTRs). Fractional-order rods also give rise to periodic peaks near integer values. Without substrate relaxation, the fractional-order rods

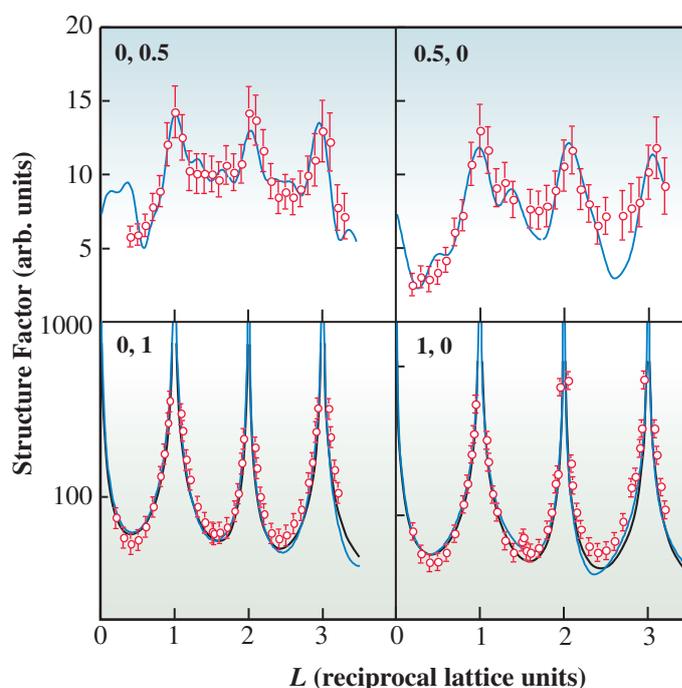


Fig. 2. Structure factors obtained from the crystal truncation rods and fractional-order rods. The blue lines are calculated structure factors obtained from the optimized model. The black lines are calculated ones for a perfectly terminated Ru(001) surface.

do not yield sharp peaks. This indicates that the deviations of Ru atoms from the bulk-phase positions in response to oxygen adsorption occur not just at the topmost surface, but also in the deeper layers. The structural refinement was performed considering the  $p3m1$  symmetry. The 9 outermost substrate Ru layers, including 36 Ru atoms and an oxygen atom were subjected to structural refinement. Each substrate layer included four Ru atoms in a  $(2 \times 2)$  unit cell. In the original paper we present the analysis procedure in detail and the atomic parameters [1].

Figure 3 shows the optimized structural model of oxygen adsorbed on the Ru(001) surface. Atomic oxygen adsorbs at the hcp hollow sites. The Ru-O bond length is 0.203(5) nm, which is consistent with the value determined by the dynamical LEED analysis [2]. The other structural parameters of the lateral and vertical displacements in the first and second layers are also consistent with DFT calculations [3] and LEED results [2]. The atomic rearrangement of the substrate reached the sixth

layer. Although it is reported that adsorbate-induced surface relaxation often occurs, the displacement from the bulk position is usually damped at the third layer in a close-packed low-index surface. Oxygen adsorption remarkably enhances the distortion of the atomic arrangement of the internal layers. Atomic displacement decreases exponentially with depth below the second layer. Previous LEED-based analyses have reported adsorbate-induced surface relaxation in the first and second layers on a number of metal surfaces with  $(2 \times 2)$ -O structures. The lateral expansion (0.006 nm) of Ru atoms (red arrows in Fig. 3) in contact with oxygen in the first layer is significantly larger than that of the others. The binding energy of O on Ru is much higher than on Pt, Pd, Ir, Ni, and Rh. The high binding energy causes the large displacement in the first layer and the large multilayer relaxation of Ru(001)- $(2 \times 2)$ -O. The high brilliance SR surface X-ray diffraction conclusively reveals that adsorbed oxygen markedly perturbs the surface electronic structure of a metal.

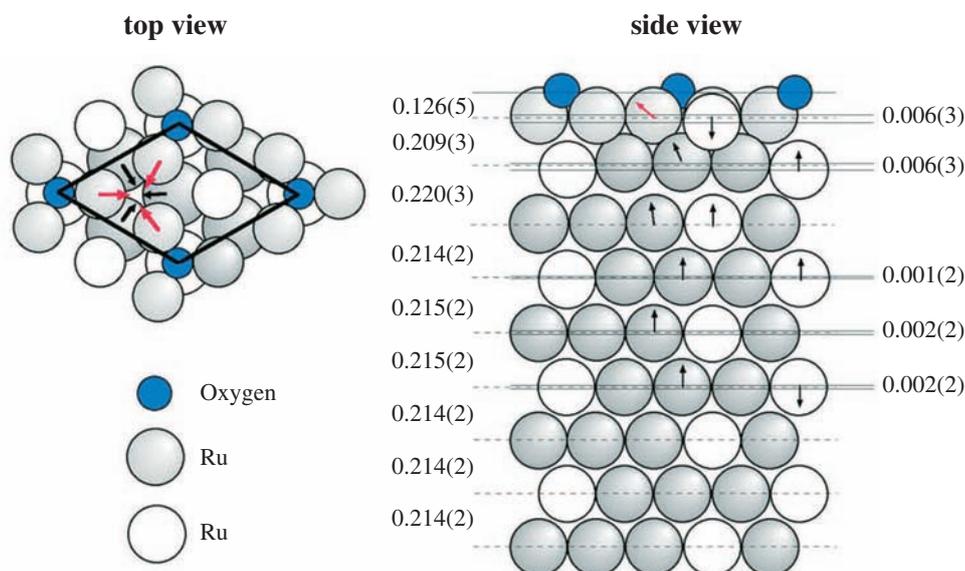


Fig. 3. Optimum surface structure for oxygen adsorbed on Ru(001). Small circles represent adsorbed oxygen atoms. Gray and white circles represent equivalent and independent Ru atoms, respectively. The dashed line indicates the position of the center of gravity in each layer.

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