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Interaction of oxygen and carbon monoxide with Pt(111) at intermediate pressure and temperature : revisiting the fruit fly of surface science

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Cover Page



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Summary

The work presented in this thesis resulted from an NWO project on the use of current transient detection of surface-catalyzed chemical reactions by means of scanning tunneling microscopy. In line with the proposed idea, the oxidation of carbon monoxide was chosen as a probe reaction and the Pt(111) surface as the catalytically active substrate. An available Omicron VT-STM system was used as the central experimental setup. In order to test the proposal, a number of additional studies had to be performed. One of these was the preparation of tunnel probes (tips) that allowed for STM experiments with stable currents for long times, as described in Chapter 2. Initial performance studies led to modification of the UHV setup and additional detailed studies of CO oxidation were needed to gain the required level of control.

Temperature has an important effect on the dissociative adsorption of molecular oxygen on platinum surfaces and thereby on CO oxidation. In Chapter 3 it was shown that, if the substrate temperature is increased to 400-600 K, the total amount of oxygen adsorbed onto Pt(111) can be more than twice the well-established maximum coverage of 0.25 ML. While LEED and STM reveal a conventional $p(2 \times 2)$ structure of the topmost layer, temperature programmed desorption measurements indicate that additional oxygen is stored under the surface of platinum. Reactivity measurements show that this sub-surface oxygen layer does not lower the activity of this platinum surface towards CO oxidation. Therefore, while a sub-surface oxygen layer does form under catalytically relevant temperatures on Pt(111), it has no great influence on the oxidizing ability of this surface. This sheds new light on the initial stages of platinum oxide formation and may help bridge the understanding of catalytic oxidation of CO on Pt in UHV and in high-pressure catalysis studies. The sub-surface oxygen is likely the precursor of the stoichiometric α -PtO₂ formed in catalytic reactors and as such links catalytic oxidation reactions in UHV and at high pressure conditions.

An increase in substrate temperature brings an additional transition phenomenon into the studied system, as was also demonstrated in Chapter 3. It is the reversible migration of adsorbed oxygen into the substrate. From this, it was concluded that the reaction at room temperature would likely have the least possible sources of unwanted noise in the current transient experiments.

In Chapter 4, catalytic oxidation of carbon monoxide on Pt(111) surface was investigated by means of STM and LEED at room temperature and a total pressure of 1×10^{-4} mbar. In this regime O_2 and CO compete for adsorption sites and, depending on the composition of the mixture, the platinum surface appears covered by a reactive ordered adlayer of atomic oxygen, by a reactive mixture of both adsorbates, or is blocked by a compact layer of adsorbed carbon monoxide. All three states were characterized and the transitions between them visualized with LEED and STM at the critical concentration of CO. In the intermediate state the platinum surface demonstrates a complex structure on the atomic scale with ordered islands of oxygen separated by regions without distinct order. While results fit well with titration studies and corresponding simulations, this “mixed” state is found to be not stable enough to sustain a continuous reaction under the conditions studied.

The analysis of current transients for a set of CO oxidation conditions that seemed appropriate from the previous studies, is presented in the last chapter of this thesis. We thus followed the original proposal for determining the noise level in the tunneling region and applied it to the $Pt(111)+O_{2(gas \leftrightarrow adsorbant)}+CO_{(gas \leftrightarrow adsorbant)}$ system. The obtained results were inconclusive, as we expected the tunneling current noise to change as a result from changes in the adsorbent composition and its atomic geometry. In the experiment, an enhanced noise amplitude was observed only in the presence of oxygen. If the system artefacts could be put aside, one would be able to conclude that the reaction rate of carbon monoxide oxidation on Pt(111), or at least the STM noise associated with it, depends on oxygen surface diffusion.