Microscopy and spectroscopy on model catalysts in gas environments
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Chapter 6

Summary and Outlook
Catalyst applications are vast and include the areas of energy supply and sustainability [2–10]. All types of catalysts increase the activity and/or selectivity of a reaction while returning back to their original state themselves [11,12]. Heterogeneous catalysts in particular are solid surfaces that catalyze gas-phase reactions. Surface science aims at understanding how such surfaces catalyze the reaction in detail on the atomic level [20]. Standard surface-science techniques such as microscopy, spectroscopy, and diffraction techniques are easiest applied on flat metal single crystals in ultra-high vacuum. As industrial catalysts function at atmospheric or even significantly higher pressures, one speaks of the pressure gap between research and application [21]. There is considerable effort in bridging this gap by developing various in situ techniques [37]. The ReactorSTM, used in Chapters 3 and 4, is a scanning tunneling microscope inside a flow-reactor cell which is incorporated into an ultra-high vacuum chamber [44]. In this way it combines the controlled preparation and characterization of model catalysts with imaging in atmospheric gas pressures revealing the structure of the catalytic surface during the reaction [46–48]. Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) on the other hand can reveal chemical states of surface atoms as well as adsorbed species during the reaction in the mbar pressure range [54]. In combination with synchrotron X-rays, as used in Chapter 5, this technique allows for high surface sensitivity, energy resolution, as well as swift measurements [230,231]. Apart from the pressure difference, industrially used catalysts also consist of multiple components with complex structures compared to single crystals studied in surface science. In order to bridge this so-called materials gap [21], model catalysts are made increasingly more complex from flat metal single crystals to stepped [22] and curved [24] single crystals, oxide single crystals [30], and metal [31], oxide [29], as well as sulfide [32] nanoparticles on top of the different single crystals. This thesis presents work on a metal single crystal, an oxide single crystal, as well as a complex model catalyst containing nanoparticles.

Chapter 3 presents a first-time use of a ZnO(1010) single crystal in the ReactorSTM. Zinc oxide is part of the most-studied catalyst for methanol steam reforming, Cu-ZnO/Al₂O₃ [72,75,76]. The use of such a catalyst in hydrogen fuel-cell vehicles could make them safer and more convenient. However, the main challenge is for the catalyst to be highly selective for producing CO₂ instead of the side product CO, for which the zinc oxide could play a significant role [79,80]. Although ZnO(1010) is a flat single crystal, we mention a number of challenges that come with its use in scanning tunneling microscopy in UHV. Among these are its affinity for H₂O adsorption from the UHV background, the incorporation of argon below the surface, and a loss of conductivity with repeated preparation, which we interpret as a loss of natural hydrogen impurities. Another experimental challenge is the amount of background water in the in situ cell of
the ReactorSTM, which we measure in detail in Chapter 3 and relate it to the design of the gas delivery system. This leads to a water pressure on the order of roughly 1 mbar when filling the cell to 1 bar total pressure of any gas. When exposing the ZnO(1010) surface to argon in the ReactorSTM, this water leads to a roughening of the surface in the form of the formation of a large number of additional steps on top of the original terraces. In this process, the formation of (0001)- and (000¯1)-type steps is favored compared to (1¯210)-type steps, which we interpret to be in contradiction with theoretical but in agreement with experimental literature. Preliminary results on the exposure of ZnO(1010) to wet hydrogen suggest that a stabilizing effect of the terraces might be able to counteract the roughening. As water is a reactant in the methanol steam reforming reaction, it has to be concluded that the (1010) face of zinc oxide might not be stable under reaction conditions and the applicability of UHV studies on ZnO(1010) as a model for the industrial process is rather limited. Although we suggest the use of dried gases to confirm the role of water, as well as studies at temperatures more relevant for the catalytic application, further use of ZnO(1010) in the ReactorSTM would first require systematic trials to improve its preparation method.

In Chapter 4 we move on to studying a more complex, yet inverted, model catalyst, TiO$_2$/Au(111), which is prepared via physical vapor deposition. Gold-based catalysts, usually applied in the form of gold nanoparticles on different oxide supports, are active for CO oxidation at lower temperatures compared to more conventional catalysts [134]. Therefore, they could reduce CO emissions during the cold start-up of combustion engine vehicles. Additionally, the lower reaction temperature allows for the selective oxidation of CO in H$_2$ environment over gold-based catalysts [131-133], which can again supply clean hydrogen for fuel-cell vehicles. However, the reaction mechanism including the oxidation state of the gold during the reaction [158-160], the role of the oxide support [34,149-153], as well as the role of water in the gas mixture [161-164] are not unambiguously identified in the current literature. First studying the Au(111) substrate in the ReactorSTM, we observe the formation of gold oxide islands under exposure to atmospheric pressures of oxygen, CO oxidation reaction conditions, or CO alone. The surface oxide can be identified by its unit cell, which is also formed when exposing Au(111) to atomic oxygen. Although the presence of oxygen on the surface can be confirmed with lab-based XPS, the surface sensitivity and energy resolution of synchrotron near-ambient pressure XPS will be necessary for the detection of oxidized gold. As the gold oxide islands observed here are always connected to a step edge of Au(111) and molecular oxygen is unlikely to dissociate by itself [171], we interpret the formation in line with the water-enabled dissociation of O$_2$ on the step edge of Au(111) as it is suggested from theoretical studies [174]. On the other hand, the presence of contaminants on the gold surface can strongly promote the gold oxide formation even
on the terraces. As background water as well as contaminants in the gold are likely present on industrial catalysts under realistic reaction conditions, it can be concluded that the presence of the oxide is likely as well. However, certain reaction studies in literature disagree on whether this would promote or rather poison the reaction [158–160]. Additionally, the exposure of TiO$_2$/Au(111) to CO oxidation reaction conditions in the ReactorSTM has revealed no difference in the gold oxide formation compared to the Au(111) substrate alone. This suggests that, although (defected) TiO$_2$ might dissociate O$_2$ [181,182], the resulting atomic oxygen does not end up on the gold substrate. Thus, the atomic oxygen spillover from TiO$_2$ to Au is not part of the CO oxidation reaction mechanism on TiO$_2$/Au(111). The ReactorSTM offers a number of opportunities to further study this system: the interaction of Au(111) with CO alone and resulting carbon depositions, the influence of a hydrogen environment on the catalyst structure including the gold oxide formation, and a comparison of TiO$_2$/Au(111) to its non-inverse counterpart, gold nanoparticles on a TiO$_2$ single crystal.

Chapter 5 of this thesis focuses on a different in situ technique, near-ambient pressure X-ray photoelectron spectroscopy, performed at Max IV [231] as well as at the ALS [230]. A cobalt single crystal is used as a model for a Fischer-Tropsch synthesis catalyst. This reaction [205] allows for the production of cleaner [208,209], synthetic fuels from syngas, a mixture of H$_2$ and CO, which can be produced from natural gas, oil, or renewable sources. Cobalt catalysts, although already used industrially [211,212], are investigated in line with a number of deactivation mechanisms [216,217] like oxidation [222–225] and the deposition of carbon, sulfur, and reaction products [218–221]. It is clear from the current state of the literature that the oxidation behavior can strongly depend on the H$_2$-to-CO ratio, the water partial pressure, as well as the structure of the cobalt sample [227,228]. As one piece to this puzzle, we thus present the first NAP-XPS results measured on Co(0001) during Fischer-Tropsch synthesis at 0.25 mbar total pressure. In this case CO seems to be more efficient at keeping the Co(0001) surface metallic than H$_2$, especially as the water background is able to oxidize the Co(0001) in H$_2$ even when a liquid nitrogen trap is used to dry the hydrogen. Although the opposite behavior is reported in lower [229] as well as higher [242] total pressure ranges, these results roughly agree with those on cobalt foil in a similar pressure range [226]. We offer a possible interpretation of the difference between the interaction of CO and H$_2$ with Co(0001) at different pressures based on their preferred adsorption and dissociation sites compared to water. Relevant for this explanation is that, in experimental studies, a Co(0001) surface cannot be perfectly flat but contains steps and vacancies. However, the picture is not yet complete and we suggest near-ambient pressure studies on Co(0001) in a larger range of gas composition, total pressure, and temperature. Additionally, Chapter 5 presents a model to convert measured spectra into coverages
on the Co(0001) surface, which is applied to quantify the adsorbed products as well as poisons during the reaction. Here, detailed carbon spectra can aid in the identification of different carbon species, hydrocarbon products, and CO adsorption sites, which should, however, be confirmed in future studies.

Although this thesis gives examples of model catalysts based on metals and oxides often used to bridge the materials gap, other materials such as alloys are not used as routinely yet. An example would be PdZn, which is a promising catalyst for methanol steam reforming [290]. PdZn can be studied with surface-science techniques when it is formed on top of zinc oxide single crystals after the deposition of palladium [291]. However, in these cases it cannot be excluded that results are influenced by the surrounding elements and the specific structure of the supported alloy. To our knowledge, there is no established method to prepare macroscopic single crystals of alloys when the melting temperatures of the two metals differ as significantly as between palladium and zinc. Currently, such a method is being developed in Leiden. It is based on an existing single-crystal face of the metal with the higher melting point, Pd(111) in the case of PdZn. The zinc is introduced in the form of a Zn rod, which is placed in a hole in the back of the Pd(111) crystal and enclosed with additional palladium. When carefully heating the crystal in ultra-high vacuum, zinc atoms will diffuse through the palladium crystal until they reach the surface. Using a surface-sensitive and spatially resolved spectroscopy technique, the formation of the alloy on the surface can then be studied as a function of the distance from the center. If the original zinc rod has a significantly smaller diameter than the palladium single crystal, the zinc-to-palladium-ratio decreases from the center to the sides of the crystal surface. This gradient could allow for a number of spatially resolved studies, like molecular beam studies and in situ spectroscopy, to shed light on the influence of the zinc-to-palladium-ratio on the catalytic activity. When successful, this method to prepare alloy single crystals could in principle be expanded to many other alloys of which no single crystals are available at the moment.

In general, the results presented in this thesis exemplify how low concentrations of contaminants in the gas phase as well as in sample materials can have a significant effect when moving from UHV to in situ studies in order to bridge the pressure and materials gaps. Often, such effects are suppressed by using very pure materials and gases, which simplifies the interpretation of data. The ReactorSTM used in Chapters 3 and 4 suffers from a large water background. Based on tests done in line with this thesis, we consider a complete redesign of the gas delivery system necessary to allow for proper drying of the gases. However, drying and purifying again reduces the relevance of the obtained results for realistic reaction conditions, which undermines the motivation for in situ surface science. Therefore, we suggest more systematic comparisons of pure
compared to non-pure studies, which can be achieved by consciously not drying gases, or intentionally adding water, and for example controllably depositing small amounts of certain contaminants onto clean samples. At the same time the behavior of complex model catalysts can only be understood well if every component is investigated separately before combining them. Additionally, it is crucial to include specific information about the gases, materials, setups, and gas delivery systems in publications to facilitate literature comparisons. The interpretation of data and comparisons of pure and non-pure studies can be especially challenging at user facilities such as those used in Chapter 5 as the user is not too familiar with the design of the gas delivery system and the possible sources of contaminants.