High-pressure STM studies of oxidation catalysis

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Summary

The main theme of this thesis is the catalytic oxidation of CO, which we have investigated on several model catalyst surfaces at atmospheric pressures and elevated temperatures with the combination of Scanning Tunneling Microscopy and Mass Spectrometry. The general background of this work was discussed in Chapter 1. In addition, this chapter provided a brief description of the technique of Scanning Tunneling Microscopy and of the employed apparatus, namely a home-built High-Pressure Scanning Tunneling Microscope.

In Chapter 2 a short literature review on the CO oxidation on Pt group metals was presented. The bonding of CO molecules to these metals, the reaction mechanisms proposed for the CO-O_2 oxidation reaction and the non-linear behavior of this reaction were introduced.

CO oxidation on low-index and vicinal palladium surfaces was studied using scanning tunneling microscopy and mass spectrometry in Chapter 3. It was shown that, when exposed to ambient pressures of oxygen at elevated temperature, these surfaces oxidize irrespective of their orientation. In this pressure regime the oxides were shown to have a higher reactivity than the metallic surfaces. The reaction mechanism on the metallic palladium surfaces follows the classic Langmuir-Hinshelwood kinetics, while the reaction on palladium surface oxides exhibits Mars van Krevelen kinetics. As a consequence of the Mars van Krevelen mechanism, the oxide surfaces were found to roughen continually. In a certain window of partial pressure combinations of O_2 and CO reaction rate oscillations were observed on Pd(100) and on its vicinal surface Pd(1.1.17). We have shown that these oscillations correspond to the periodic switching of the surface between the metallic state with the Langmuir Hinshelwood reaction and the oxidic form with the Mars van Krevelen reaction.

A literature overview was given in the first part of Chapter 4 on various models describing the observed oscillatory behaviour of CO oxidation on Pt group metals. In the second part of Chapter 4 we introduced a completely new explanation for the oscillatory CO oxidation on palladium surfaces, which is based on two key features: (1) the observation that the oxide surface gradually roughens under reaction conditions and that the metal surface gradually smoothens and (2) the relation between the surface roughness and the CO partial pressure at which the surface switches between metal and oxide (and vice versa).

Chapter 5 presented our results for the CO-O_2 reaction at atmospheric pressure and elevated temperatures on Pt(111). CO adsorption was found to lead to the formation of a regular overlayer structure, identified as $(\sqrt{19}\times\sqrt{19})$ R23.4°-13CO. The stability of this structure under different reaction conditions was discussed. These results were further used to illustrate the importance of temperature in a catalytic system. We showed that at elevated temperatures Pt(111) oxidizes in an O_2-rich gas mixture and that the oxide has a higher reactivity than the metallic surface, similar to the palladium surfaces of Chapter 3. Also oscillations in the reaction rate were observed.

Chapter 6 was devoted to CO oxidation on Pt(100). In contrast with the other surfaces studied in this thesis, the clean Pt(100) surface exhibits a phenomenon called surface reconstruction. We found that exposure to either O_2 or CO lifts this reconstruction. In an O_2-rich flow and at elevated temperatures Pt(100) was observed to oxidize. Under these reaction conditions the oxide was only marginally more active than the metal surface and in most cases no difference could be observed at all between the reaction rates under conditions where both states of the surface were stable. However, since the metallic surface could be exposed to much higher CO partial pressures, spectacularly high conversion rates could be achieved on that surface. A second bistability was observed in this high-CO-pressure regime, which was identified as the traditional Langmuir-Hinshelwood bistability.

In addition to this investigation of the oxidation of CO by O_2 on various model catalyst surfaces we have briefly explored two related reaction systems, which were presented in the two appendices. In Appendix I we discussed preliminary results on the catalytic oxidation of CO by NO (or equivalently the catalytic reduction of NO by CO) on Pt(100), which show that the reaction rate depends strongly on the temperature and the catalyst structure.

The partial oxidation of ethylene on Ag(111) has been studied briefly in Appendix II. The results suggest that under reaction conditions the active catalyst might be a tick, insulating silver oxide. In addition, the complete oxidation of ethylene on Pt(111) at 1.25 bar and elevated temperature confirmed that the reaction follows a Langmuir-Hinshelwood type of mechanism.