A comparative study of platinum nanodeposits on HOPG (0001), MnO(100) and MnOx/MnO(100) surfaces by STM and AFM after heat treatment in UHV, O2 , CO and H2

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Chapter 7

Summary and recommendations for further research of the model catalytic systems described in this thesis

This thesis is focused on the study of the morphology of Pt deposits on HOPG and MnO(100) surfaces using scanning probe techniques - STM and AFM. The Pt/HOPG system with a range of Pt coverages was annealed under UHV and in the presence of low pressures of oxygen, carbon monoxide and hydrogen. Based on the size distributions of platinum nanoparticles, suggestions were made concerning the sintering mechanism of this metal on the HOPG surface.

A considerable part of the research was devoted to finding ways to prepare single-phase manganese oxide surfaces, preferably smooth and well-defined, that are suitable to study platinum deposits on the surface. As a starting point a MnO(100) surface was chosen. The preparation of a model manganese oxide support was carried out by means of annealing of the MnO(100) surface under UHV, and in the presence of argon and oxygen at a range of temperatures and gas partial pressures. The resulting surfaces were analyzed by several techniques. Specifically, the topography of the samples was examined by AFM and STM. X-ray diffraction was employed to find out to what extent transformation of MnO phase takes place after a specific temperature treatment. XPS was used to identify the average oxidation state of manganese in an as-received and in some annealed MnO(100) samples. The issue of the near surface region stoichiometry of some samples was addressed by use of RBS.

Platinum deposition was performed on an as-received and on an altered MnO(100) surface by annealing in oxygen and hydrogen.

The formation of surface morphologies found on the MnO(100) surface in the course of the study, e.g., the rippled-like structure and trapezoid-like pillars, need a detailed examination and more experiments are necessary to understand the origin, composition and evolution of these structures. It is believed that such information can be obtained by the use of a range of complementary techniques.

Taking into account the specific properties of the manganese oxide system and literature data concerning the vast list of techniques that are used at present for surfaces characterization, several techniques are proposed for future studies to resolve the structure-morphology-evolution questions.

In line with conventional XRD used in the present study to measure the bulk composition of manganese oxide, *grazing incidence X-ray diffraction* (GIXRD) [1, 2] could be employed to find out the composition of the near surface region (1-2 nm). Using synchrotron radiation the sensitivity of this technique can

be further increased.

X-ray Absorption Spectroscopy (XAS) proved to be a highly sensitive technique for identifying the valence state of transition metals [3]. The shift of the threshold energy can provide information about the valance state of an absorbing atom [3, 4]. Considering this, two regions of the XAS adsorption spectrum, the first one in a region between the Fermi energy and about 30 eV above the Fermi energy (so-called *X-ray absorption near edge structure, XANES*), and the second - above the XANES region (*extended X-ray absorption fine structure*, EXAFS) can provide information about the oxidation state and are sensitive to the short range order of an atom even in complex and disordered systems [4]. Conventional EXAFS technique can be made more surface sensitive by using grazing incidence, and by varying the incidence angle, the surface sensitivity can be increased to the nm scale. Usage of synchrotron X-ray radiation of high intensity further extends the potential of identifying element's oxidation state. This technique has already been applied to analyze some manganese oxide species [5-12].

The elemental composition of model manganese oxide surfaces can be probed as well by using *low energy ion scattering* (LEIS) that is exclusively sensitive to one atomic layer because of the high neutralization probability of the noble gas ions [13, 14]. In addition, it is known that the shape of the background contains information about the vertical distribution of elements in the near surface region.

By using *electron energy loss spectroscopy* (EELS) it is possible to probe lattice vibrations of the substrate or electronic transitions that are excited with monochromatic low energy electrons [15]. The energy resolution is much better than in X-ray spectroscopy, and as a result more structural information can be obtained from the fine structure in EELS. Within facilities capable to irradiate a support with electrons, as e.g., scanning transmission electron microscope (STEM) or transmission electron microscope with energy filter [16], EELS can deliver information on composition and electronic structure of the surface phases. In addition, EELS combined with these microscopic techniques has advantages compared to other spectroscopies to provide spectra from sub-nanometer scale area [17]. Ionization edges in the EEL spectrum contain fine structures [called the *energy-loss near edge structure* (ELNES)] and provide information about the electronic structure of specimens. The positions of the oxygen K and so-called white lines L_2 and L_3 of manganese as well as their intensity ratio, $I(L_3)/I(L_2)$ in the core-loss EELS spectrum are characteristic of the oxidation state of manganese ions in manganese oxides specimens [18].

Registering lattice vibrations by means of *high resolution energy loss spectroscopy* (HREELS), can help in resolving the surface composition problem of manganese oxide surfaces. The technique allows to measure spectra with a

resolution of *ca*. 2 meV [13]. Specifically, different manganese oxides could be detected by this technique owing to its capability to register surface optical long wavelength phonons, so-called Fuchs-Kliewer (FK) phonons, which are of distinctly different energy than the bulk phonons. The HREEL spectrum of poorly conducting transition metal oxides shows an intense surface phonon structure with multiple phonon excitations. In particular, a HREEL spectrum of rocksalt monoxides, to which MnO also belongs, due to its high symmetry usually shows intense single loss features with additional losses at integral multiples of the single-loss peaks and with intensities decreasing in a Poisson distribution. The MnO phase exhibits a series of FK multiple phonon excitations with single fundamental loss energy at 70.9 meV [19] and multiple excitations at integral values of the fundamental phonon loss energy. Since other manganese oxides possess lower symmetry than the MnO phase, their appearance on the surface is immediately reflected by changes in HREEL spectra. According to Langell *et al.* [19], the second phonon loss of the Mn_3O_4 phase mode appears as a distinct peak at 55.6 meV. However, HREELS might not permit to establish the composition of the very near surface region of manganese oxides due to the large probing depth of several hundred Ångströms (in semiconductors) and a long decay length of the FK phonons [20]. Thus, in principle the combined application of HREELS and SPM techniques could deliver a great deal of information for establishing the correlation between chemical composition and morphology of the surface.

Various kinds of vibrational spectroscopy techniques such as surface *Raman scattering* and *Fourier transform-infrared* (FT–IR) spectroscopy, the theoretical background of which can be found, for example, in [13, 21] can also be of aid in differentiating between the manganese oxides [22, 23]. The spectra of various manganese oxides display bands which are diagnostic for their Mn-O skeleton and structural arrangement of basic MnO_6 units. The differences in the vibrational modes of manganese oxides are mainly attributed to the edge-sharing of the MnO_6 octahedra, intrinsic distortion of the basic MnO_6 octahedron and to some extend to the variations in average manganese oxidation states. The vibrational modes of the MnO_6 units expand over 400-650 cm^{-1} and there are several bands in the low-wave length region [22]. Owing to distinct patterns in this region by using Raman spectroscopy, a direct discrimination between the species is possible.

Special information about the symmetry of the surface structures of manganese oxides, a kind of data that is inaccessible by other surface science techniques can be obtained by more extensive use of LEED [3].

Selected area (electron) diffraction (SAED) [24] is a crystallographic experimental technique similar to X-ray diffraction that can be performed inside a transmission electron microscope (TEM). It permits to sample the area as small as several hundred nanometers and is used to identify crystal structures and examine

crystal defects. However, this method of analysis suffers from the common TEM requirement to prepare very thin samples with a thickness of about 100 nm. Thus, it would be quite difficult nevertheless possible to implement it to manganese oxide analysis.

Finally, for establishing the structure correlations of different manganese oxide phases on the MnO(100) surface as well as for the investigation of the Pt-MnO interaction, theoretical calculations, with, e.g., density functional theory methods [25] would be of great importance.

In conclusion, I would like to note that the techniques employed in the presented work allowed only the post-treatment examination of the surfaces. Pursuing further research it would be interesting to perform *in-situ* real time SPM imaging of the studied model catalytic systems under similar conditions which were employed in the present work. Such experiments would directly answer the questions regarding the evolution of structural changes on the surface. In future studies of manganese oxide based model catalysts it would also be interesting to image other surfaces of MnO and surfaces of other manganese oxides. It is believed that for this purpose, besides synthetically grown single-crystals, one may also use some of the naturally occurring manganese oxide species, for example Mn_2O_3 and Mn_3O_4, which can form well-defined large enough crystals. It is hoped that Pt deposition on different manganese oxide surfaces and investigation of such model systems under different environments by scanning probe techniques, as well as techniques proposed in this section, can deliver a wealth of information on the interaction between this metal and manganese oxide phases.

7.1 References

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