High-pressure STM studies of oxidation catalysis

Bobaru, Ş.C.

Citation

Bobaru, Ş. C. (2006, October 25). *High-pressure STM studies of oxidation catalysis*. Retrieved from https://hdl.handle.net/1887/4952

Chapter 1

Introduction

In this chapter the relevance of surface science studies to applied heterogeneous catalysis is discussed. The technique of Scanning Tunneling Microscopy (STM) and our experimental set-up for STM under high-pressure conditions are also described.

1.1 Heterogeneous catalysis

Berzelius has given the name “catalysis” in 1836 to a branch of chemistry that employs compounds, called catalysts, which accelerate chemical reactions without being consumed in the process. Catalysis has a great impact on our society. Without catalysts most chemical reactions used in today’s chemical plants and for environmental protection would proceed so slowly that they could not even be detected, even when the reaction conditions (e.g. temperature and pressure) make the reactions thermodynamically favourable. In addition to their importance in the chemical and petrochemical industry, catalysts play a role in the preservation of our environment, by converting polluting waste gases into less harmful products [1]. A catalyst speeds up the reaction by lowering one or more activation barriers or by introducing an alternative reaction path with lower energy barriers. It is important to remember that the acceleration of reactions is not the only key factor in catalytic activity. Catalysts are designed not only to *accelerate* reactions; they also should be *selective*. In other words, a catalyst should speed up the right reaction, not simply every reaction. As a consequence, the activation barrier for the desired product should be decreased much more than the barriers for other, undesired products [2].

Catalysis can be classified into various types. One important type of catalysis is homogeneous catalysis where the catalyst and the reactants exist in the same phase. Two prime examples of homogeneous catalysis are the condensation of esters to polyesters and the hydroformulation of alkenes to aldehydes (solvents, detergents, alcohols). Biocatalysis forms another important branch of catalysis. In this discipline, enzymes are used as biochemical catalysts. One of the most common reactions in this field is photosynthesis. When the reactants and the catalyst are present in different phases, one speaks of heterogeneous catalysis. Heterogeneous catalysis plays a key role in the large-scale production of plastics, liquid fuels, fertilizers, pharmaceuticals and many other every-day chemicals. Another important application is pollution control, in particular in the automotive industry [3-4]. Within heterogeneous catalysis the most common reactions are those in which the reactants and the products are in the gas phase while the catalyst is in the solid phase. Due to the fact that mass transport processes in the solid phase are slow compared to the reaction rates, the chemical reaction usually takes place at the gas-solid interphase, i.e. at the surface of the solid catalyst. The work presented in this thesis is related to heterogeneous catalysis.

1.2 The three-way catalyst

One of the best-known important applications of heterogeneous catalysis is the three-way catalyst, which is used to efficiently remove harmful components from the exhaust gas of car engines. This catalyst has high rates for the conversion of three different types of gases, namely NO_x, CO and hydrocarbons. These gases have harmful effects either for human health or for the environment. CO is poisonous. The oxides of nitrogen contribute to acid rain, low level ozone and smog formation, which exacerbate breathing problems [3-4]. The hydrocarbons are also involved in the formation of smog. The main reactions, which are important for controlling exhaust emissions, are given by the following stoichiometric equations:

$$\mathrm{CO+\tfrac{1}{2}O_2 \rightarrow CO_2} \tag{1}$$

$$\mathrm{Hydrocarbons+O_2 \rightarrow H_2O+CO_2} \tag{2}$$

$$\mathrm{NO+CO \rightarrow \tfrac{1}{2}N_2+CO_2} \tag{3}$$

$$\mathrm{H_2+\tfrac{1}{2}O_2 \rightarrow H_2O} \tag{4}$$

$$\mathrm{NO+H_2 \rightarrow \tfrac{1}{2}N_2+H_2O} \tag{5}$$

On the basis of the above reactions the final products should be harmless: N_2, CO_2 and H_2O. These reaction products are thermodynamically favored at typical exhaust temperatures, e.g. 770 K. The three-way catalysts contain the noble metals platinum, rhodium and often palladium. Rhodium exhibits excellent activity for the selective reduction of NO to N_2, only a small amount of Rh being required in the composition of the three-way catalyst. Platinum is used for its contribution to the conversion of CO and hydrocarbons. Palladium plays a similar role. Therefore, commercial three-way catalysts for gasoline engines are often a bimetallic combination of two of these precious metals, e.g. Pt-Rh or Pd-Rh [3, 6-7].

1.3 Surface-science studies

The discipline that deals with the processes taking place on the surface of a solid is called “surface science”. It is important to realize that the structure and electronic properties of the surface of a solid are very often different from those of the rest of the solid, the bulk. Related to this also the binding energy for many atoms and molecules at surfaces is different from the equivalent energies in the bulk, and, hence, the chemical properties of the surface are special. In particular, the presence of dangling bonds, uncoordinated atoms, and special sites (at e.g. steps, kinks and point defects) makes the surface a very attractive place for strong chemical interactions. Studies of heterogeneous catalytic systems by means of surface-science tools aim to answer a variety of important, fundamental questions, such as:

(a) How do catalysts work at the atomic or molecular scale?
(b) What are the active sites of a solid catalyst?
(c) What are the intermediate compounds that form at the surface during a catalytic cycle?
(d) How does the morphology of the catalyst surface change during the reaction?

In order to characterize the relevant structural, electronic and chemical properties of a catalytic system a wide range of surface sensitive techniques has been developed over the last decades. Here, we mention just a few of them. The surface chemical composition can be probed by Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), and secondary ion mass (SIMS) spectroscopy. Techniques like low energy electron diffraction (LEED), surface X-ray diffraction (SXRD), low-, medium- and high- energy ion scattering (LEIS, MEIS and HEIS), thermal energy helium atom scattering (HAS), and photoelectron diffraction (XPD), constitute useful tools for determining the surface structure. Additional information about the geometry of the surface can be obtained by scanning and transmission electron microscopy (SEM and TEM), field-ion microscopy (FIM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Surface vibrational properties can be investigated with infrared spectroscopy (IR), Raman spectroscopy, high-resolution electron energy loss spectroscopy (HREELS) and sum frequency generation (SFG) [8-11]. In addition knowledge about the surface composition and atomic geometry is provided by the ‘ab initio’ methods e.g.: the density functional theory (DFT), the Lattice-gas Hamiltonian, the recently introduced “Wang-Landau” algorithm or the Monte Carlo (MC) simulations. Such methods should quantitatively describe measurable properties without relying on experimental parameters, which implies that they have to start ab initio, e.g., from the self-consistent evaluation of the electronic structure. They provide detailed insight in the electronic rearrangements that lead to bonding and bond breaking. They also give estimations for the energies and energies barriers accompanying these processes [12-14]. The application of these techniques has resulted in important progress in understanding the fundamentals of surface chemistry and catalysis.

In spite of these achievements there are two significant drawbacks of these ‘traditional’ surface science studies that strongly affect their relevance to the understanding of many practical catalytic systems. The first one arises from the so-called “pressure gap”, which indicates that in industry catalytic processes are usually performed at relatively high pressures (1-100 atm), whereas typical surface-science studies are carried out under well-controlled vacuum conditions. The second discrepancy is that a heterogeneous industrial catalyst almost invariably has a complex structure, whereas only simple model systems (usually single crystals) are used in most surface-science laboratories. This problem is often referred to as the” materials gap”. A growing effort has been made in the last decade to bridge these two gaps. Concerning the “materials gap”, examining not only the simplest flat surfaces, but also the kinked or stepped surfaces, represents a small step in this context [15]. Another way to tackle the problem is to use metal alloys [16]. Also an increasing number of studies are devoted to more elaborate model systems that reproduce some of the complexity of a practical catalyst, in the form of an ensemble of metal catalyst particles deposited on flat supports of oxides or other, well-defined substrates [17].

In order to overcome the “pressure gap” several types of surface-science instruments have been re-designed in order to enable them to acquire data “in situ” under more realistic (or less unrealistic) conditions, such as higher pressures and higher temperatures [18-21]. As we have mentioned already, the difference between the pressures used in the traditional surface-science research (10^{-10} to 10^{-4} mbar) and the pressures used in typical industrial processes (1-100 bar) is more than 10 orders of magnitude. The pressure of the gas phase plays a weak role in the thermodynamics of the gas-surface interaction via the chemical potential. For example, the chemical potential of oxygen atoms depends as follows on the partial pressure of oxygen molecules in the gas phase and on temperature:

$$\mu_{\mathrm{O}}(T,p)=\mu_{\mathrm{O}}\left(T,p^{0}\right)+\tfrac{1}{2}k_{B}T\ln\left(p/p^{0}\right) \tag{1.1}$$

where p^0 is the standard pressure [22], k_B is Boltzmann constant, while μ_{O} stands for the chemical potential. This means that if the oxygen pressure p changes for example by a factor 10^{10}, the chemical potential changes by $23k_BT$. Although the pressure has only a logarithmic (i.e. weak) effect, it adds up to a significant change in the chemical potential of e.g. 0.3 eV per atom at room temperature over these 10 orders of magnitude. This has the consequence that an oxygen-rich adsorption structure that is energetically unfavorable under ultrahigh vacuum (UHV) conditions might be stabilized by the presence of the high-pressure gas phase.

1.4 Scanning tunneling microscopy and catalysis studies

1.4.1 Introduction

Since its invention in 1981 by Binning, Rohrer, Gerber and Weibel [23], Scanning Tunneling Microscopy has had a tremendous impact on the development of surface science. First of all, it enabled the study of the atomic structure of conducting surfaces, with atomic resolution in real space. Secondly, it had a great influence on the study of homo- and heteroepitaxial thin film growth by investigating growth process at atomic scale [24]. In the last decade STM has also become a powerful technique for the characterization of physical and chemical processes involved in heterogeneous catalysis.

In short, the Scanning Tunneling Microscopy technique can be described as follows. If a sharp, conducting needle (tip) is brought within a few atomic distances from a conducting surface, quantum mechanics predicts that there is a probability for electrons to jump from the tip to the surface and vice versa: the tunneling effect. By applying a voltage V between the tip and the surface, a current I can be generated, which depends exponentially on the distance between the tip and the surface d:

$$I \propto V \exp(-2\kappa d), \tag{1.2}$$

where in simple approximation κ is given by $\sqrt{2m\Phi/\hbar^2}$. Φ is the average work function of the tip and the sample and $\hbar = h/2\pi$, where h is Planck's constant. The strong exponential dependence of the tunnel current on the distance between the tip and the sample leads to extremely high resolution in the STM measurements. The STM experiments in this thesis have been performed in so-called 'constant-current mode', which means that a feedback system has been active to continually adjust the height of the tip in order to keep the tunnel current constant. In order to obtain a topographic map of the surface the tip must be rastered or scanned back and forth across the surface. The resulting STM image can then be viewed as a height map of constant density of electronic states at a fixed energy difference with respect to the Fermi energy E_F. The instrument can also be used for spectroscopic purposes by temporarily freezing the position of the tip and recording a spectrum of the tunneling current as a function of the tip-substrate voltage. Such an I-V spectrum provides local information on the electronic structure of the surface [25-26].

In order to meet the requirements for the STM investigation of catalytic systems under realistic conditions, i.e. high pressure, high temperature and flowing gas mixtures, several new ideas have been implemented with respect to the 'classic' design of a scanning tunneling microscope. In the next section we introduce some of the details of our high-pressure scanning tunneling microscope, an innovative design which has allowed us to study catalytic systems under reaction conditions, at elevated temperatures and high pressures.

1.4.2 Our set-up

In this section we briefly introduce the apparatus that was used for the acquisition of the STM data presented in this thesis. A full description of the set-up can be found in previous publications of our group [27-28]. The most important components of our set-up are (1) the main UHV chamber, (2) the high-pressure, flow-reactor STM cell, which is integrated into the main chamber, (3) the sample holder, and finally (4) the gas handling system which allows dosing of highly purified gases mixed in adjustable ratios into the high-pressure cell. We refer to the high-pressure STM cell as the 'Reactor-STM'.

Main chamber

The main UVH chamber has a cylindrical shape and was made from a massive block of stainless steal. The UHV system is mounted in a frame supported on four vibration isolations legs. The base pressure of $1x10^{-10}$ mbar is achieved and maintained by the use of a combination of turbomolecular, ion getter and titanium sublimation pumps. In order to minimize the vibrations introduced by the pumping, a turbomolecular pump with magnetic bearings has been selected. The UHV chamber is divided in two parts, separated by a UHV manual gate valve. One part is used as the *preparation* chamber, where the sample is prepared and characterized by the means of traditional UHV techniques. For surface preparation there is an ion gun in combination with a high-purity Argon gas inlet for Ar^+ ion bombardment. The sample can be annealed to temperatures of approximately 1200 K with the filament mounted at the back of the sample by radiative heating and electron bombardment. For cleaning purposes a high-purity oxygen inlet is also attached to the chamber. In order to investigate the surface structure and composition before and after the high-pressure exposure this side of the chamber is equipped with a combined low-energy electron diffraction /Auger electron spectroscopy (LEED/AES) system. The Reactor–STM is situated in the other part of the main chamber, the *reactor* side. Except for the Reactor-STM, which is described below, the reactor side contains a quadrupole mass spectrometer (QMS). The QMS is used for residual gas analysis in the UHV system and for the analysis of the composition of the gas that leaves the reactor. As will be explained later, the reactor is closed via a replaceable Kalrez seal [29]. This part of the UHV chamber also contains a storage cassette for replacement of damaged Kalrez seals. By use of a wobble stick, located directly above the reactor cell, we can easily replace these seals without breaking the vacuum. The sample can be rotated and moved through the vacuum chamber by a linear transfer rod contained in a bellow. The movement of the transfer rod is driven by an external electromotor. The transfer rod contains electrical connections and wiring for heating the sample and temperature measurements. Some of the heating elements for vacuum bake out are mounted on the individual vacuum components. Other heating elements have been integrated in the walls of the vacuum chamber. All pumps and gate valves of the main chamber are controlled by a home-built electronic control system.

Reactor-STM

Figure 1.1 shows a schematic representation of the reactor-STM. It mainly consists of a small (400 µl) cylindrical shaped reactor. The reactor walls are gold plated in order to avoid any interference of the walls in the investigated chemical reaction. From one side the reactor is closed by the polished surface of the sample. A thin plate of Kalrez acts like a seal between the polished surface of the sample and the reactor edges. The lower side of the reactor volume is closed by pressing an aluminum tube, which is closed at the bottom side, against a flexible Viton O-ring. This tube is connected to the piezo element of the STM and is used to carry the STM tip. The Viton ring is sufficiently flexible to allow the scanning motion. The piezo element is placed outside the reactor, while the tip (Pt/Ir alloy) is situated inside the reactor. Two gas lines: an inlet and an outlet are attached to the reactor. It should be stressed here that the reactor is not sealed perfectly. In particular, the flexible Kalrez seal constitutes a small leak into the UHV chamber. We put this continuous leak to good us, since it enables us to perform real-time analysis of the gas composition in the reactor during the high-pressure experiments, by use of the quadrupole mass spectrometer.

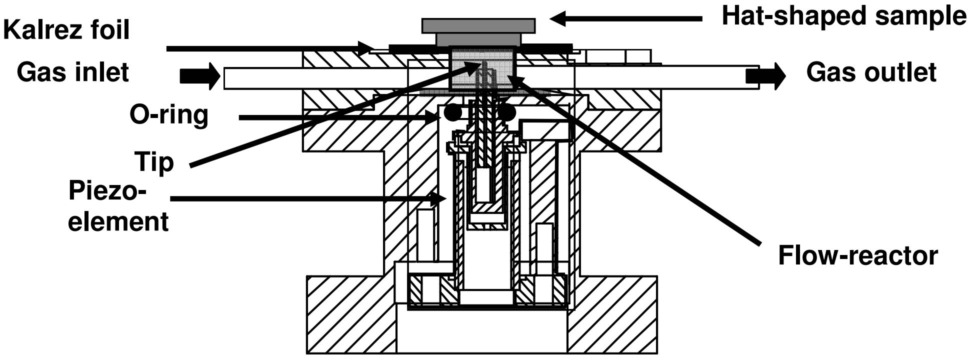

Figure 1.1: *Schematic cross section of the Reactor-STM combination*

Sample holder

The sample holder carries a hat-shaped sample, which is suspended in a tantalum ring. The design of the sample holder has been done in such a way that it allows heating of the sample both in the flow-reactor and on the transfer rod in the UVH chamber. The heater that is mounted at the back of the sample, in two ceramic plates, consists of a tungsten filament from a commercial halogen light bulb. For focusing purposes during the electron bombardment a quartz tube surrounds the filament. A chromel-alumel thermocouple (pressed directly against the back of the sample), which is electrically isolated by a ceramic tube, provides measurements of the temperature. The sample holder has two wings that slide into clamps when it is placed above the reactor cell. These clamps are used to pull the sample holder down, so that the sample is firmly pressed against the Kalrez seal and closes off the reactor. Since even the compressed Kalrez is somewhat flexible, it forms a deformable element in the mechanical loop between the tip and the sample and thus makes the STM sensitive to vibrations, which limits the spatial resolution. In some of the experiments described in this thesis, we have used a metal support structure between the sample surface and the reactor to close the mechanical loop directly after a few hundred μm compression of the Kalrez seal. This greatly reduced the sensitivity to external vibrations and allowed us to obtain higher-resolution images, as is demonstrated e.g. in Chapter 5 and 6 of this thesis.

Gas handling system

The Reactor-STM inside the UHV chamber is attached to a gas manifold, which has the possibility of pre-mixing a maximum three high-purity gases with the use of mass-flow controllers and pressure regulators. This dedicated gas system consists entirely of stainless steal components. The pressure in the reactor (200 mbar up to 5 bar) is kept constant, independent of the flow settings, via a pressure regulator located in the exit gas line from the reactor. The mass flow controllers can sustain a constant flow between 0-20 ml per minute. In most of the measurements described in this thesis the flow rate have been 3ml$_n$/min.

1.5 This thesis

The aim of this thesis is to gain insight into chemical reactions taking place under atmospheric pressures and elevated temperatures. We have made use of the Reactor-STM described above, which is a combination of a flow reactor and an STM. With this instrument we have examined the relation between the structure of metal model catalysts and their catalytic activity. A short introduction concerning CO bonding to transitional metals and the mechanisms proposed for CO oxidation on platinum group metals is given in Chapter 2. Chapter 3 concentrates on the CO oxidation reaction over low- and high-index palladium surfaces, Pd(100), Pd(1.1.17) and Pd(553). We find that by switching from a CO-rich flow to an O_2-rich flow we can reversibly oxidize and reduce the palladium surface for each of these surface orientations. The reaction on the metal surface proceeds always by the Langmuir-Hinshelwood mechanism. By contrast, the reaction on the oxide occurs via a Mars van Krevelen type of mechanism. In the reaction kinetics, bistability is observed and oscillations in the reaction rate. We determine the experimental conditions for the oscillations and study the influence of catalyst structure, and in particular the effect of steps on the reaction rate. In Chapter 4 a mechanism is proposed for the reaction rate oscillations described in Chapter 3. Chapter 5 describes CO oxidation at atmospheric pressure on the Pt(111) surface, which proceeds similarly to that on Pd(100). In Chapter 6 we learn more about the reaction between CO and O_2 over the (100) surface of platinum. Pt(100) exhibits the so-called quasi-hex reconstruction. The effect of both gases CO and O_2 on the reconstructed structure is discussed. The differences in reactivity between Pt(111) and Pt(100) are also highlighted. Preliminary observations for two very important reactions are briefly presented in Appendix I (NO reduction by CO over Pt(100)) and Appendix II (ethylene epoxidation). The results in these appendices have didactical value and could constitute a basis for future experiments.

1.6 References

[1] J. H. Sinfelt, *Surf. Sci.* **500** (2002) 923.

[2] K. W. Kolansinski, *Foundations of catalysis and nanoscience*, John Willey and Sons, LDT 2001.

[3] B. E. Nieuwenhuys, *Adv. Catal* .**44** (1994) 259.

[4] H. P. Bonzel, *Surf. Sci.* **68** (1977) 236.

[5] http://www.platinum.matthey.com/applications/autocatalyst.html

[6] K. C. Taylor, Automobile catalytic converters, Springer, Berlin, 1984.

[7] Society of Automotive Engineers, *Cold-start emission control and catalyst technologies*, SAE International, 1996.

[8] F. Zaera, *Prog. Surf. Sci.* 69 (2001) 1.

[9] J. W. Niemantsverdriet, Spectroscopy in Catalysis: An Introduction, Wiley-VCH, 2000.

[10] G. A. Somorjai , Introduction to Surface Chemistry and Catalysis, Wiley-Interscience, 1984.

[11] G. Attard and C. Barnes, *Surfaces,* Oxford University Press, 1998.

[12] C. Stampfl, M. V. Ganduglia-Pirovano, K. Reuter, M. Scheffer, *Surf. Sci.* **500** (2002) 368.

[13] S. Yip (Ed.), *Handbook of material Modelling, Fundamental Models, Methods,* Vol.1, Kluwer, 2005.

[14] C. Stampfl, *Catalysis Today* **105** (2005) 17.

[15] H. Y. Hirano, K. Tanaka, J. Siera , and B. E. Nieuwenhuys, *Surf. Sci.* **222** (1989) L804.

[16] E. Backus, PhD. Thesis, Leiden University, The Netherlands, 2005.

[17] A. M. de Jong et al., *J. Phys. Chem.* **97** (1993) 6477.

[18] H. Bluhm, D. F. Ogletree, C. S. Fadley, Z. Hussain, and M. Salmeron, *J. Phys.:Condens. Matter* **14** (2002) L227.

[19] T. W. Hansen, J. B. Wagner, P. L. Hansen, S. Dahl, H. Topsoe, and C. J. H. Jacobsen, *Science* **294** (2001) 508.

[20] X. Su, P. S. Cremer, Y. R. Shen, and G. A. Somorjai, *Phys. Rev. Lett.* **77** (1996) 3858.

[21] P. Bernard, K. Peters, J. Alvarez, and S. Ferrer, *Rev. Sci. Instrum.***70** (1999) 1478.

[22] K. Reuter and M. Scheffler, *Phys. Rev. B* **65** (2002) 035406.

[23] G. Binning, H. Rohrer, Ch. Gerber and E. Weibel, *Phys. Rev. Lett.* **49** (1982) 57.

[24] M. Bischoff, PhD. Thesis, Nijmegen University, The Netherlands, 2002.

[25] R. Wiesendanger (Ed.), *Scanning Probe Microscopy and Spectroscopy:Methods and Applications,* Cambridge University Press, 1994.

[26] R. Wiesendanger (Ed.), *Scanning Probe Microscopy: Analytical Methods (Nanoscience and Technology),* Springer, 1998.

[27] P. B. Rasmussen, B. L. M. Hendriksen, H. Zeijlemaker, H. G. Ficke and J.W.M. Frenken, *Rev. Sci. Instrum.* **69** (1998) 3879.

[28] B. L. M. Hendriksen, PhD. Thesis, Leiden University, The Netherlands, 2003.

[29] Kalrez perfluorelastomer, DuPont Dow elastomers L.L.C.; Eriks, Alkmaar, The Netherlands