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# KATALYTICKÉ SYSTÉMY ZALOŽENÉ NA JEDNOTLIVÝCH ATOMECH

SINGLE ATOMIC CATALYSTS

DIPLOMOVÁ PRÁCE MASTER'S THESIS

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# Zadání diplomové práce

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Ředitel ústavu Vám v souladu se zákonem č.111/1998 o vysokých školách a se Studijním a zkušebním řádem VUT v Brně určuje následující téma diplomové práce:

## Katalytické systémy založené na jednotlivých atomech

#### Stručná charakteristika problematiky úkolu:

Experimentální práce věnovaná popisu stability a schopnosti jednotlivých atomů na površích vázat, příp. aktivovat či disociovat, molekuly plynů. Práce zahrnuje přípravu vzorků v UHV a jejich analýzu pomocí STM a XPS.

#### Cíle diplomové práce:

1. Stručně popište základní principy přípravy povrchových struktur schopných vázat jednotlivé atomy a použité experimentální metody.

2. Experimentálně popište interakci plynu s jednoatomárními katalyzátory.

#### Seznam literatury:

H. Lüth: Surfaces and Interfaces of Solid Materials, Third ed., Springer-Verlag, Berlin 1997.

Termín odevzdání diplomové práce je stanoven časovým plánem akademického roku 2015/16

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## Abstrakt

Realizace katalytických systémů založených na jednotlivých atomech umožní dosáhnout limitních vlastností kvality a selektivity katalyzátorů při současném zvýšení jejich životnosti a snížení celkových nákladů. Klíčovou vlastností katalyzátorů je jejich schopnost zachytit reaktanty a následně snížit energetickou náročnost chemické reakce. Tato práce se zabývá prvně jmenovaným: interakcí plynů (H<sub>2</sub>O, CO, O<sub>2</sub> a NO) s jednotlivými atomy kovů (Rh, Ir, Cu) na povrchu magnetitu. Hlavní experimentální technikou je rastrovací tunelová mikroskopie umožňující studium povrchů na atomární úrovni.

## Abstract

Single atom catalysts are prospective class of materials, which holds promises to reach the ultimate limit of improvement in catalyst performance, selectivity, lifetime and cost reduction. The ability to efficiently capture the adsorbates at the active sites is the key prerequisite for catalytic transformation to the products. In this respect, our experimental study aims to describe the interaction of gas molecules (H<sub>2</sub>O, CO, O<sub>2</sub> and NO) with single metal atoms (Rh, Ir, Cu) on the magnetite surface employing scanning tunneling microscopy.

## Klíčová slova

jednoatomové katalyzátory, magnetit, rhodium, iridium, měď, železo, kyselina tereftalová, samouspořádaní, STM.

## Keywords

single atom catalysts, magnetite, rhodium, iridium, copper, iron, terephthalic acid, self-assembly, STM.

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Bc. Adam Závodný

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# 1. Introduction

Catalysis pervades the global economy and is very important in production of many goods that are crucial for the humanity such as fuels, chemicals, food, plastics and pharmaceuticals [1–6]. Even minor improvements in the catalyst performance could cause major cost savings in their industrial production. The development of more energy efficient and environmentally friendlier catalysts is a challenge for the scientific community in these times of depleting natural resources and increased environmental concerns. This work is dedicated to the emerging field of single atom catalysis (SAC), which promises reduced costs coupled to dramatic improvements in catalyst efficiency, selectivity and lifetime [7,8].

Nowadays, supported metal nanoparticles are the most widely used type of heterogeneous catalyst in industrial processes. Unfortunately, the best catalysts tend to be the rare and expensive metals such as Pt and Rh. The size of metal particles is a key factor in determining the performance of such catalysts. Only low-coordinated metal atoms usually function as the catalytically active sites, therefore enormous efforts have been devoted towards improving the performance of supported metal catalysts by downsizing the metal particles, i.e., increasing the specific activity per metal atom. The downsizing of metal particles can induce the complete change in their behaviour. Very nice example is gold (Au), which is inert as bulk material, but becomes catalytically active when the size of nanoparticles reaches 10 nm and less [9]. This enhanced activity is usually attributed to the electronic effects, but can also be caused by different metal-support interaction.

However, the supported metal catalysts generally consist of an assembly of metal particles with broad size distributions and irregular morphology, therefore each metal particle can have multiple active sites with different performances. Such heterogeneity affects the efficiency of catalytic performance leading to the reduced selectivity towards a specific catalytic reaction. These problems solve single atom catalysts (SACs), which are the ultimate small-size limit for metal nanoparticles. SACs consist of isolated metal atoms singly dispersed on supports. All metal atoms are accessible to reactants and high activity and selectivity can be achieved in this way.



Figure 1.1: Comparison of resolution achievable by (a) TEM with our (b) STM. Both images show metal adatoms  $(a - Pt_1 \text{ and } b - Rh_1)$  supported by iron oxide. TEM image was taken from [7].

#### 1. INTRODUCTION

It has been reported that SACs really do work [10–13]. But there is little atomic-scale information available to better understand how these processes occur. Currently, High Resolution Transmission Electron Microscopy (HRTEM) is the method used by chemists for studying SACs. This technique barely reaches the resolution high enough to see both metal atoms (Fig. 1.1) and more importantly adsorption sites or the coordination environment of catalytically active metal atoms. Therefore, in this work the Scanning Tunnelling Microscopy (STM) was used to achieve sufficient atomic resolution. The chapter 2 of presented master's thesis is dedicated to this technique.

It is well known that supported metal atoms have a strong intrinsic tendency to agglomerate into bigger clusters. This makes the preparation of SACs very challenging. We studied two model catalysts prepared by two different approaches, i.e., molecular selfassembly of metal atoms and organic molecules on metal surfaces and the direct adsorption of metal atoms on a support strongly binding these metal atoms, thus preventing them from agglomeration into clusters. The preparation of systems studied in this master's thesis is described in the chapter 3.

For a catalyst, the ability to efficiently capture the adsorbates around the active site is the key criterion for catalytic performance. The experimental study of interaction of single metal atoms with gas molecules, e.g., CO, O<sub>2</sub>, H<sub>2</sub>O, NO, CO<sub>2</sub>, is the main aim of this master's thesis. The experimental results are presented and discussed in the experimental part (chapters 4, 5, 6 and 7).

# 2. Scanning Tunneling Microscopy

In a 1959 speech entitled *There's Plenty of Room at the Bottom* [14], Richard Feynman invited scientists to a new field of research: to see individual atoms distinctly, and to arrange the atoms the way we want. Feynman envisioned that, by achieving those goals, one could synthesize any chemical substance that the chemist writes down, resolve many central and fundamental problems in biology at the molecular level, and dramatically increase the density of information storage. Some 20 years later, those goals began to be achieved through the invention and application of the scanning tunneling microscope (STM) [15–17] and the atomic force microscope (AFM) [18]. The inventors of STM, two physicists at IBM Research Division, Gerd Binnig and Heinrich Rohrer, shared the 1986 Nobel Prize in physics [19, 20].

Being the ubiquitous apparatus for nanoscience, the range of phenomena studied by STM is continuously growing. The measurement of surface topography, the investigation of ground state properties of excitations, vibrational [21], magnetic [22–25] or optical [26] properties, which allow chemical identification of atoms, and even the measurement of their magnetic anisotropy energy are today major topics studied with state-of-the-art machines. Recently, magnetometry measurements allowed to extract quantitative values for magnetic exchange interactions among adatoms separated by large distances [27, 28]. Also other applications and developments of STM aim towards the measurements of adhesion and strength of individual chemical bonds, friction, studies of dielectric properties, contact charging, molecular manipulation and many other phenomena from the micrometer down to subnanometer scale.

## 2.1. Instrumentation

Before discussing the basic theory explaining the measurements that can be done with STM, a description of this tool is needed. The schematic picture of a scanning tunneling microscope is shown in Fig. 2.1. A crucial ingredient in any STM is the probe tip that is attached to a piezodrive, which consists of three mutually perpendicular piezoelectric transducers (x, y, and z piezo). Upon applying a voltage, a piezoelectric transducers contract or expand, which allows to move the tip over the surface. Upon applying a bias voltage, V, between the tip (which is not touching the substrate) and sample, a weak current I flows via a tunneling mechanism through the vacuum when the tip is very close to the sample.

The most straightforward way of operation of the scanning tunneling microscope is the direct measurement of the variation of the tunneling current as a function of the scanning position while keeping the distance between tip and sample surface constant. In this way, a so-called constant height image is obtained. However, the usual procedure is to keep the tunneling current constant while scanning over the surface. This is done by changing the distance between the tip and surface using a feedback loop. Here, the voltage at the piezoelectric crystal is adjusted to give the set tunneling current and the distance from sample is recorded. One obtains then the so-called constant current STM image. The STM can also be used for the tunneling spectroscopy measurements. It is usually done by interrupting the feedback in order to keep the tip-sample distance constant for the I-V spectroscopy data acquisition. This can be done at any desired surface position.

#### 2.1. INSTRUMENTATION

The resolution of STM image is limited by the radius of curvature of the scanning tip. Additionally, image artefacts can occur if the tip is doubled, i.e., the probe tip ends with two points and both of them contribute to the tunneling current. Therefore, it has been essential to develop processes for consistently obtaining sharp, usable tips. The tip is often made of tungsten or platinum-iridium, though gold is also used. Tungsten tips are usually made by electrochemical etching, and platinum-iridium tips by mechanical shearing.

Due to the extreme sensitivity of tunneling current on the tip-sample distance, a proper vibration insulation or an extremely rigid STM body is imperative for obtaining usable results. In the first STM by Binnig and Rohrer, magnetic levitation was used to keep the STM free from vibrations; now mechanical or gas spring systems are often used.

Maintaining the tip position with respect to the sample, scanning the sample and acquiring the data is computer controlled. The computer may also be used for enhancing the image with the help of image processing.



Figure 2.1: Schematic description of scanning tunneling microscope. The picture was adapted from [29].

## 2.2. The concept of tunneling

Here, we describe briefly elementary theories of tunneling through a one-dimensional potential barrier, which will help us to grasp the basic concepts used in STM. In quantum mechanics, the state of electron in a potential U(z) (see Fig. 2.2), is described by a wave function  $\psi(z)$ , which satisfies the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\psi(z) + U(z)\psi(z) = E\psi(z).$$
(2.1)

In this elementary model, the STM is simplified to a one-dimensional potential barrier where the vacuum is modelled by the potential barrier  $U_0$ , while its left and right sides represent the sample, S, and the tip, T, respectively. For  $E < U_0$ , the general solution of Eq. 2.1 for potential barrier U(z) shown in Fig. 2.2 is:

$$\psi_S = Ae^{ikz} + Be^{-ikz},\tag{2.2}$$

$$\psi_{Barrier} = Ce^{-\kappa z} + De^{\kappa z},\tag{2.3}$$

$$\psi_T = F e^{ikz} + G e^{-ikz},\tag{2.4}$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} > 0 \quad \text{and} \quad \kappa = \frac{\sqrt{2m\left(U_0 - E\right)}}{\hbar} > 0. \tag{2.5}$$



Figure 2.2: Simple one-dimensional potential barrier, which explains the physics of tunneling. When the two electrodes are far apart, the wave functions of both electrodes T (tip) and S (sample) decay into the vacuum while the tunneling can take place if the electrodes are closer.

For the electron moving from left (in +z-direction) and amplitude of incident wave A = 1, there can be only the wave propagating in +z-direction in the tip electrode T, hence the coefficient G = 0 in Eq. 2.4.

The coefficients B, C, D and F are obtained by matching of the wave functions and their derivatives  $d\psi/dz$  at the two interfaces, sample-barrier and barrier-tip. Incident  $\psi_i$ and transmitted waves  $\psi_t$  are given by

$$\psi_i = e^{ikz}$$
 and  $\psi_t = F e^{ikz}$ , respectively. (2.6)

## 2.2. THE CONCEPT OF TUNNELING

The current density is defined as

$$J = -i\frac{\hbar}{2m} \left( \psi^*\left(z\right) \frac{d\psi\left(z\right)}{dz} - \psi\left(z\right) \frac{d\psi^*\left(z\right)}{dz} \right).$$
(2.7)

Using Eqs. 2.6 and 2.7 we can calculate the incident and transmitted current density  $(J_i$  and  $J_t$  respectively):

$$J_i = \frac{\hbar k}{m}$$
 and  $J_t = \frac{\hbar k}{m} |F|^2$ . (2.8)

The incident and transmitted current density define the barrier transmission coefficient T which is given by the ratio between the transmitted current density and the incident current density:

$$T = \frac{J_t}{J_i} = |F|^2 = \frac{1}{1 + \frac{(k^2 + \kappa^2)^2}{4k^2\kappa^2} \cdot \sinh^2(\kappa s)},$$
(2.9)

which simplifies in the limit of a strongly attenuating barrier (large decay constant  $\kappa$ )

$$T \sim \frac{16\kappa^2 k^2}{(k^2 + \kappa^2)^2} \cdot e^{-2\kappa s},$$
 (2.10)

where s defines the tip-sample distance (see Fig. 2.2).

From this simple one dimensional model one can derive the principle used by Binnig and Rohrer when they invented the STM. Their argument to explain the ability of STM to achieve small lateral resolutions and by that to probe the electronic structures of various materials at an atomic scale ( $\sim 2 \text{ Å}$ ) is: because of the tunneling through vacuum, the lateral resolution much smaller than the radius of the tip-end, R, is possible if the distance between the tip-end and the sample surface,  $\Delta z$ , is much smaller than the tip radius [30]. Near the tip-end, the current lines are almost perpendicular to the sample surface (see Fig. 2.3).



Figure 2.3: Estimation of the lateral resolution in STM. Out of a spherical tip model with radius R very close to the surface, the lateral resolution of STM can be evaluated. The tunneling current is concentrated at the vicinity of the closest point to the substrate.

#### 2. SCANNING TUNNELING MICROSCOPY

If we take a point on the tip shifted by  $\Delta x$  from the tip-end, the distance of this point from the sample surface, z, is by

$$\Delta z \sim \frac{\Delta x^2}{2R} \tag{2.11}$$

bigger than the distance of the tip-end to the sample surface. Assuming that at each point the tunneling current density follows the formula for the one-dimensional case, Eq. 2.10, the lateral current distribution is

$$I(\Delta x) \sim e^{-2\kappa \frac{\Delta x^2}{2R}}.$$
(2.12)

Typically,  $\kappa \sim 1\text{\AA}^{-1}$ . For R = 10 Å, at  $\Delta x \sim 4.5$  Å, the current drops by a factor of  $\sim e^{-2}$ , that is about one order of magnitude. The diameter of such a current column is the resolution limit, which is about 9 Å. Nowadays, achievements of STM largely exceed this expectation. We need more realistic model of the tip to theoretically describe the resolution in recent STM studies.

## **2.3.** Theory of $STM^1$

In the previous section the basic principles of tunneling of electrons through the finite potential barrier were explained. Unfortunately, the real theory behind the STM is very complicated. Therefore, several approximations have to be used to obtain equations for the tunneling current which permit practical computations and help us to interpret the STM images.

The tunneling current is given to the first order in Bardeen's formalism by

$$I = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} f(E_{\mu}) \left[1 - f(E_{\nu} + eV)\right] |\mathbf{M}_{\mu\nu}|^2 \,\delta(E_{\mu} - E_{\nu}), \qquad (2.13)$$

where f(E) is the Fermi-Dirac function, V is the applied voltage,  $\mathbf{M}_{\mu\nu}$  is the tunneling matrix element between states  $\psi_{\mu}$  of the probe and  $\psi_{\nu}$  of the surface, and  $E_{\mu}$  is the energy of state  $\psi_{\mu}$  in the absence of tunneling. Note that while Eq. 2.13 resembles ordinary first-order perturbation theory, it is formally different in that  $\psi_{\mu}$  and  $\psi_{\nu}$  are nonorthogonal eigenstates of different Hamiltonians. Since the experiments are performed at room temperature or below and at small voltages (for metal-metal tunneling), we take the limits of small voltage and temperature,

$$I = \frac{2\pi}{\hbar} e^2 V \sum_{\mu,\nu} |\mathbf{M}_{\mu\nu}|^2 \,\delta\left(E_{\nu} - E_F\right) \delta\left(E_{\mu} - E_F\right).$$
(2.14)

In handling of Eq. 2.14 in general, the essential problem is to calculate  $\mathbf{M}_{\mu\nu}$ . In [33] it has been shown that

$$\mathbf{M}_{\mu\nu} = \frac{\hbar^2}{2m} \int d\mathbf{S} \cdot \left( \psi^*_{\mu} \bigtriangledown \psi_{\nu} - \psi_{\nu} \bigtriangledown \psi^*_{\mu} \right), \qquad (2.15)$$

where the integration is performed over all surfaces lying entirely within the vacuum (barrier) region separating the two sides. The quantity in parentheses is simply the current operator.

<sup>&</sup>lt;sup>1</sup>The articles [31, 32] were used as a source for this section.

#### 2.3. THEORY OF STM

Now, we consider the limit where the tip is replaced with a point probe. The tip is represented by a mathematical point source of current at point  $\mathbf{r}_t$ , i.e., no electronic structure of the tip is taken into account. We can make this approximation because it can be shown that during tunneling, the closest atom to the surface is the main one involved in the tunneling process. Moreover, this approximation represents the ideal measurement of the surface with the maximum possible resolution. If the tip wave functions are arbitrarily localized, the matrix element is simply proportional to the amplitude of  $\psi_{\nu}$  at the position  $\mathbf{r}_0$  of the probe, and Eq. 2.14 reduces to

$$I \propto \sum_{\nu} |\psi_{\nu} \left( \mathbf{r}_{0} \right)|^{2} \delta \left( E_{\nu} - E_{F} \right).$$
(2.16)

The quantity on the right side of Eq. 2.16 is simply the surface local density of states (LDOS) at  $E_F$ . Thus the tunneling current is proportional to the surface LDOS at the position of the point probe, and the STM image represents a contour map of constant surface LDOS (in constant current operation mode).

# 3. Preparation of single atom catalysts

A huge problem for SACs is the intrinsic tendency of metal atoms to agglomerate into bigger clusters. The prevention from sintering (agglomeration into clusters) can be achieved by several different approaches. Two methods of preparation of SACs were used in this thesis. The first part of this chapter is dedicated to the approach, which utilizes a support that strongly binds metal atoms in particular adsorption sites. The Fe<sub>3</sub>O<sub>4</sub>(001) (magnetite) single crystal is appropriate support for this application. The second part of this chapter deals with the application of molecular self-assembly of metal atoms and organic molecules on metal surfaces for preparation of SACs. In contrast to the first method, this one is more time-consuming, but advances in chemistry synthesis allow to tailor the atomic structure of organic molecules providing a very wide range of flexibility in electronic structure, thus it has a huge potential for the design of single atom catalysts.

## 3.1. Magnetite(001) surface

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is a naturally abundant oxide material in the environment and its surfaces play an important role in environmental redox reactions, corrosion processes and geochemistry. Its magnetic properties were discovered in approximately 1500 BC, which makes it the earliest known magnet.

Moreover, Fe<sub>3</sub>O<sub>4</sub> is utilized in many industrial applications where surface properties are critical including catalysis [34, 35] and groundwater remediation [36]. The fact that Fe<sub>3</sub>O<sub>4</sub> is a room temperature half-metal [37] has led to attempts to incorporate it as a ferromagnetic electrode in spintronic devices, but the performance of device prototypes has been disappointing [38–40] due to the ill-defined nature of the Fe<sub>3</sub>O<sub>4</sub>/semiconductor interface [41, 42].



Figure 3.1: The inverse spinel  $Fe_3O_4$  bulk unit cell containing O (red), tetrahedral  $Fe_{tet}$  atoms (cyan) and octahedral  $Fe_{oct}$  atoms (yellow). The picture was adapted from [43].

The bulk  $Fe_3O_4$  has the inverse-spinel structure with  $Fe^{3+}$  cations in tetrahedral sites and a 1:1 mixture of  $Fe^{2+}$  and  $Fe^{3+}$  in octahedral sites (see Fig. 3.1). The (001) surface of magnetite has the  $(\sqrt{2} \times \sqrt{2})R45^{\circ}$  surface reconstruction. This symmetry was observed in low energy electron diffraction (LEED) [44, 45]. The rows of surface  $Fe_{oct}$  (and O) atoms aligned in [110] direction are characteristic for this surface reconstruction. Density

## 3.1. MAGNETITE(001) SURFACE

functional theory/based calculations (DFT+U) find pairs of surface  $Fe_{oct}$  atoms relaxed in opposite directions perpendicular to the row (see Fig. 3.2). This is consistent with the undulating rows of  $Fe_{oct}$  observed in STM images [46,47].



Figure 3.2: (a) Perspective and (b) top views on the minimum-energy structure of the new model of  $(\sqrt{2} \times \sqrt{2})$ R45° reconstruction of the Fe<sub>3</sub>O<sub>4</sub>(001) determined by DFT+U calculations. The possible adsorption site is marked by a yellow cross in the figure (b). The figures were taken from [48].

The  $(\sqrt{2} \times \sqrt{2})$ R45° surface reconstruction of Fe<sub>3</sub>O<sub>4</sub>(001) is based on subsurface cation vacancies, where two Fe<sub>oct</sub> atoms from the third layer are replaced by an interstitial Fe<sub>int</sub> atom with tetrahedral coordination in the second layer [48]. Thus we have single adsorption site in the surface unit cell (see Fig. 3.2(b), yellow cross). The existence of one adsorption site per unit cell was also confirmed by our experimental studies.

This model was published in 2014, but the scientists studied this surface for decades. The DFT calculations for the former model (without cation vacancies) showed the existence of two equivalent adsorption sites per unit cell (see 3.3). Moreover, the undulation of surface  $Fe_{oct}$  rows was smaller than the undulation observed in the STM images.



Figure 3.3: (a) Perspective and (b) top views on the minimum-energy structure of the former model of  $(\sqrt{2} \times \sqrt{2})$ R45° reconstruction of the Fe<sub>3</sub>O<sub>4</sub>(001) determined by DFT+U calculations. The possible adsorption sites are marked by green crosses in the figure (b). The figure (a) was taken from [48].

#### 3. PREPARATION OF SINGLE ATOM CATALYSTS

The existence of a single adsorption site per unit cell turns the Fe<sub>3</sub>O<sub>4</sub>(001) surface into the perfect template for adsorption of single metal atoms with extraordinary thermal stability (in some cases up to 400 °C) suitable for the study of catalytic reactions [49–52]. The mutual distance between adsorbed metal atoms is ~0.84 nm. We will refer to this adsorption site as *narrow site*, because it appears in STM images for commonly used bias voltages narrower than the another one, despite the fact, it is actually geometrically wider. This phenomenon is caused by the distortion of electronic orbitals, resulting in a density of states that is asymmetric about the atom core position. This distortion is diminished at higher bias voltages. The higher bias gives a more realistic indication of the atomic core positions. The blocked adsorption site will be referred to as a *wide site*. The example of metal atoms (Au) deposited on Fe<sub>3</sub>O<sub>4</sub>(001) surface is shown in Fig. 3.4. Metal adatoms bind to surface O atoms at positions without the second-layer Fe<sub>tet</sub> atoms.



Figure 3.4: Au adatoms bind to surface O atoms at positions without second-layer  $Fe_{tet}$  atoms. This results in a nearest-neighbour Au distance of 8.4 Å. The figure was taken from [49].

# 3.2. Experimental details of $M_1/Fe_3O_4(001)$ model catalyst preparation

The general approach in  $M_1/Fe_3O_4(001)$  model catalyst<sup>1</sup> preparation is very straightforward. The preparation consists of only two steps, i.e., cleaning of the surface and the chosen metal deposition.

The experiments were performed using a natural single crystal Fe<sub>3</sub>O<sub>4</sub>(001). Its dimensions were  $1 \times 1 \text{ cm}^2$ . As the first step, the crystal was cleaned in a preparation chamber with base pressure lower than  $10^{-10}$  mbar by cycles consisting of sputtering with Ar<sup>+</sup> ions ( $p_{\text{Ar}} = 8 \times 10^{-6}$  mbar, high voltage = 1 kV, sputtering current = 2 µA , t = 10 min) followed by annealing with electron beam heating (T = 873 K, t = 30 min).

The crystal was cleaned overnight. This process was programmed and during the whole night the argon pressure in a chamber was kept at constant value  $p_{\rm Ar} = 8 \times 10^{-6}$  mbar using thermovalve. To clean the crystal we usually used 9 – 11 cycles, which was always

<sup>&</sup>lt;sup>1</sup>The M stands for metal. In this work we studied three metals: Rh, Ir and Cu.

enough to get well defined clean surface. The last annealing cycle (usually done in the morning) was always carried out in oxygen atmosphere ( $p_{O_2} = 5 \times 10^{-7}$  Torr – measured with quadrupole mass spectrometer (QMS), t = 20 min), because after many sputtering-annealing cycles the surface is reduced and we get the iron terminated surface [43]. To recover the ( $\sqrt{2} \times \sqrt{2}$ )R45° reconstruction back we had to do the last annealing cycle in this way. The surface was always checked with STM after cleaning.

Metal atoms were deposited on a freshly cleaned surface at room temperature using an Omicron triple pocket electron beam evaporator. The evaporator was cooled with liquid N<sub>2</sub> to keep the pressure in the chamber in  $10^{-10}$  mbar region. A water cooled quartz crystal microbalance (QCM) was used for the calibration of the deposition rate. The usual deposition rate was ~0.6 ML per min. 1 ML was defined as one adatom per Fe<sub>3</sub>O<sub>4</sub>(001)- $(\sqrt{2} \times \sqrt{2})$ R45° reconstruction unit cell ( $1.42 \times 10^{18}$  atoms/m<sup>2</sup>). Immediately after deposition the crystal was transferred to adjacent chamber with base pressure  $7 \times 10^{-11}$  mbar. This chamber is equipped with XPS, AES, LEIS, LEED and the major technique used in this work – STM (customized Omicron µSTM). The STM was operated in constant current mode at room temperature. All images presented in this work were acquired at room temperature. In all cases when heating is mentioned, the sample was cooled afterwards and then we started with STM measurements. The deposited metal coverage was determined by counting the number of adatoms per surface area in STM images.

## 3.3. Self-assembly of organic molecules at metal surfaces

Self-assembly is the autonomous organization of components into patterns or structures without human intervention. Self-assembly phenomena are processes common in a wide range of systems, featuring different interactions and different scales, from molecular to planetary [53]. Within this thesis the description of self-assembly of molecular systems on metallic surfaces under ultra-high vacuum conditions will be discussed.

Molecular self-assembly has been recognised as a promising route to build complex structures from molecular building blocks with atomic precision. Especially at solid surfaces, extended, two-dimensional molecular layers are already widely used, providing well-controlled properties such as corrosion resistance, surface superhydrophobicity, or antifouling coatings [54–56].

However, molecular self-assembly bears the potential for engineering much more advanced structures with high degree of complexity. Recently it has been demonstrated that molecular self-assembly can be employed to fabricate surface structures ranging from clusters [57], unidirectional rows [57–59] to porous networks with well-defined pore size and periodicity [60, 61] or arrays of metal atoms [62]. This exceptional flexibility opens up another emerging field of application, namely molecular electronics that is believed to be the successor of today's electronics based on silicon technology.

The key criterion for molecular self-assembly is the existence of predefined building blocks that interact weakly in order to provide the possibility for both bond formation and bond breaking until the stable equilibrium structure is formed. In many cases, the system may not be able to reach the equilibrium state but might be trapped in a kinetically limited state. This in most cases leads to the unorganized system, but sometimes we can get the self-organized system [63]. The difference between molecular self-assembly and

## 3. PREPARATION OF SINGLE ATOM CATALYSTS

self-organisation is illustrated in Fig. 3.5. The ratio between molecular flux and surface diffusivity needs to be considered to distinguish between molecular self-assembly and self-organisation. If the flux is high and surface diffusivity low, the molecules are not able to reach their equilibrium structure, but rather get trapped in a diffusion limited state. On the other hand, if the flux of molecules is low and the diffusivity is high, the molecules are able to move freely on the surface, resulting in the growth of the thermodynamically favoured, equilibrium structure.



Figure 3.5: Schematic illustrating the difference between self-organisation and self-assembly (adapted from [63]).

The structure formation is governed by the delicate interplay between intermolecular and molecule-substrate interactions. The diffusivity of the molecules on the surface can be controlled by a variation of substrate temperature. Upon increasing the substrate temperature, thermal energy is transferred to the molecules, thereby the molecules with sufficient thermal energy  $E_{\text{therm}}$  to overcome the diffusion barrier  $E_{\text{d}}$  on the surface (see Fig. 3.6). This is one prerequisite for the formation of the thermodynamic equilibrium structure. On the other hand, the thermal energy of the molecules  $E_{\text{therm}}$  must not exceed the binding energy  $E_{\rm b}$  of the molecules on the surface, otherwise the molecules would desorb from the surface. Finally, we need to consider the intermolecular interaction energy  $E_{\text{inter}}$ . This interaction is crucial for the formation of ordered structures as it comprises the information on how to assemble the predefined building blocks. As mentioned above, the intermolecular interaction should be "weak", meaning that the molecular entities must possess sufficient energy to probe the corrugation of the energy landscape in order to identify the equilibrium structure in the global minimum. If the intermolecular interaction is "strong" the molecules stick together irreversibly once they have met, preventing the formation of an ordered equilibrium structure. On the other hand, the interaction between the molecules must be strong enough to allow the formation of a stable structure. The second condition can be achieved when the intermolecular interaction energy  $E_{\text{inter}}$  is of the same order as the thermal energy of the molecules  $E_{\text{therm}}$ , being only slightly larger than  $E_{\text{therm}}$ . The energy conditions to be fulfilled for molecular self-assembly can therefore be summarized as  $E_{\text{b}} > E_{\text{inter}} \ge E_{\text{therm}} > E_{\text{d}}$  [64].



Figure 3.6: For molecular self-assembly to occur, the energies involved ( $E_{\rm b}$  binding energy of the molecules to the surface,  $E_{\rm d}$  diffusion barrier of the molecules on the surface,  $E_{\rm inter}$ intermolecular interaction energy,  $E_{\rm therm}$  thermal energy of the molecules) must obey the energy condition  $E_{\rm b} > E_{\rm inter} \ge E_{\rm therm} > E_{\rm d}$  (adapted from [64]).

An additional aspect needs to be considered when the molecules can both physisorb and chemisorb on the surface. Usually diffusion barriers become very large when molecules chemisorb onto the surface as chemisorption is stronger than physisorption. Therefore, an ordered structure of chemisorbed molecules on a substrate surface is usually not governed by intermolecular interactions but solely by the strong chemisorption energy. This is why molecules covalently bound to the substrate are usually not considered as molecular selfassembled structure, but rather as a "classical" superstructure (typical examples are atoms or small molecules like oxygen or carbon monoxide on various metal surfaces forming regular superstructures) [64]. However, molecular self-assembly of species chemisorbed to the substrate is possible in special cases, for example when the chemisorbed molecule together with the bound substrate atom forms a new entity, which then can diffuse and act as a new building block [65].

Besides the energetics discussed above, also the molecular building blocks can be tailored for creating well-defined molecular structures. Organic molecules as building blocks provide a wide range of variety regarding both strength of interaction as well as directionality. Moreover, they can be synthesised with great flexibility and control.

Among the versatile synthesis strategies, one of the most promising paths is provided by coordination chemistry, exploiting the interaction of organic molecules (also called *ligands*) with metal centers. Metal-ligand bonding offers a set of directional bonds of

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intermediate strength that is exploited to realize distinct geometric shapes. Moreover, coordination chemistry has gathered a vast database of metal-ligand pairs with a huge variety of specific binding modes giving the possibility to program selectivity and directionality directly into the binding motifs (see Fig. 3.7), allowing for the self-assembly of supramolecular architectures, e.g., polygonal clusters, polyhedra, cages and grids [66–69]. Therefore, the use of transition metal centers, or in general secondary building blocks, and coordination chemistry for directing the formation of complex structures has evolved into one of the most widely used strategies for organizing molecular building blocks into supramolecular frameworks [70].



Figure 3.7: Library of coordination motifs explored in surface-confined metal-ligand systems. Organic molecules with aromatic backbones enforce a flat adsorption configuration, i.e., with the ligands'  $\pi$ -systems parallel to the surface plane. The functional endgroups include carboxylate, pyridine, hydroxyl, and carbonitrile. The motif used in this study is marked by a red rectangle (adapted from [70]).

The definition of coordination systems is not trivial and encounters difficulties. In general a given coordination system consists of a coordinating atom (coordination center) ligated to other atoms or groups of atoms (ligands) by coordination bonds. In particular, for transition metal compounds the spatial distribution of the d orbitals realizes the delocalization of the one-electron bonding orbitals [71]. The actual orbital overlap between the central atom and the ligands is rather low compared to covalent bonds, of the order of 10%, but the delocalization of the electrons involving partially unoccupied (anti-) bonding ligand orbitals via charge donation and backdonation effectively reduces the Coulomb repulsion energy between the electrons and results in appreciable binding. Thus, the formation of a given supramolecular shape is driven by the inherent symmetry of the coordination sites available on the metal center, which depends on the d orbital occupation. Therefore, careful consideration must be given to the preferred coordination environment of the metal to be used and the binging mode of the linkers. Given such a coordination environment around the metal centers, the symmetric and rigid extension of the ligand system from mono- to multiplicity will automatically lead to a grid-like 1D, 2D, or 3D coordination network with regularly arrayed metal ions. The supramolecular shape is encoded in both the metal ions and in the organic ligands and the interpretation of this information during the self-assembly process leads to a mutually acceptable structure.

## 3.4. SYSTEM OF STUDY AND INTRODUCTION TO EXPERIMENT

The principles of using metals with predetermined coordination numbers and angles as building block and functional units is not only an appealing method from the point of view of synthetic chemistry. Transition metal ions incorporated in such structures do not merely act as stabilizing agent of the structures but remain accessible for the construction of more complex structures, including open networks that can host appropriate guest species. Furthermore, they possess multiple electronic/spin states and a related variety of redox, photochemical, and magnetic properties. The aim of this thesis is to use these properties for the study of single atom catalysis, in particular, the interaction of metal centers with gas molecules.

## 3.4. System of study and introduction to experiment

Our study is based on self-assembled molecular systems at surfaces focused on adaptive metal-ligand coordination networks and their functionalization with catalytically active metal atoms. The aim of this experimental study is to synthesize a stable surface-confined structure consisting of single transition metal ions accessible for catalytic reactions. To achieve this goal an organic molecule – terephthalic acid (further called TPA) is used as a ligand in supramolecular network. The molecular structure of TPA molecule is depicted in Fig. 3.8.



Benzene-1,4-dicarboxylic acid

Figure 3.8: Molecular structure with highlighted functional parts of the organic molecule used in our studies.

Terephthalic acid is a commodity chemical. This white solid is used principally as a precursor to the polyester (PET) production. The molecules of TPA consists of two basic functional groups, or *moieties*:

(1) Phenyl ring ensures a flat orientation of the molecule on the metal surface. The bonding of aromatic systems with metallic substrates is mediated by their  $\pi$  electrons

which hybridize with metallic states of the substrate; this includes electronic donation to the substrate [72].

(2) The carboxylic end-groups are utilized for the construction of supramolecular network. To make the network more robust, metal-ligand coordination is employed. Compared with covalent bonds, the coordination ones are of a lower strength, making them ideal for self-assembled systems – they are strong enough to render the network stable and, simultaneously, weak enough to allow the error correction (the ability of elimination of transiently formed defective structures, i.e., to break the bonds that do not present an ideal structure with lowest energy). We have used iron as coordinating atoms since it forms a stable iron dimer coordination motif with carboxylate ligand.

The preparation of our metal-organic structures is schematically depicted in Fig. 3.9. The whole process starts with the cleaning of the sample by cycles of ion sputtering and annealing, followed by the deposition of organic molecules (TPA) and metal atoms (Fe) onto the sample at room temperature. The final step is annealing of the sample to promote self-assembly of the desired structure. Despite the fact, that self-assembly is autonomous process resulting in equilibrium structures, it is crucial to not bring additional kinetic barriers during the preparation. The deposition of metal before the organic component is a good example. The reason is that metal atoms have intrinsic tendency to form clusters immediately after the deposition on bare surface. Since these atoms are strongly bound there, significantly higher temperatures are required for their release. The organic molecules are usually decomposed at these temperatures which makes the self-assembly process impossible. If we used lower temperatures the whole self-assembly rate would be limited by slow detachment kinetics from the metal clusters.



Figure 3.9: The schematic depiction of the preparation of metal-organic networks.

3.4. SYSTEM OF STUDY AND INTRODUCTION TO EXPERIMENT

# 4. $Rh/Fe_3O_4(001)$ model catalyst

This chapter is dedicated to the  $Rh/Fe_3O_4(001)$  model catalyst. Firstly, we show that  $Fe_3O_4(001)$  surface can accommodate Rh single atoms coexisting with Rh dimers. The presence of Rh species on the surface was confirmed by XPS. The measured Rh 3d peak is shown in Fig. 4.1. The Rh  $3d_{5/2}$  peak is shifted to a higher binding energy compared to the position associated with metallic rhodium (307.2 eV – red vertical line in XPS spectrum) by  $\sim 0.5 \,\mathrm{eV}$ , which suggests that deposited material does not form islands. To get atomic level insight, we studied the appearance of rhodium species by STM. Afterwards, we proceeded with the study of their real-time behaviour using STM movies. It is known that metal atoms deposited on  $Fe_3O_4(001)$  diffuse into the subsurface layers or into the bulk upon heating. The threshold temperature for this process varies with the type of metal atoms. For example, for gold atoms it is 450 °C [49]. Our experiments showed that  $Rh/Fe_3O_4(001)$  model catalyst is not as thermally stable as  $Au_1/Fe_3O_4(001)$ . Very low amount Rh atoms is embedded into the subsurface even at room temperature, where they are incorporated in two different configurations. The rest of this chapter deals with the experimental study of the interaction of the  $Rh/Fe_3O_4(001)$  model catalyst with gases, e.g.,  $H_2O$ , CO,  $O_2$  and NO. We found out that water dissociates after the adsorption on the surface.  $O_2$  and NO adsorption induces sintering of  $Rh_1$  adatoms into clusters, and in case of CO, only adsorption on Rh dimers was observed.



Figure 4.1: The Rh 3d peak of  $Rh_1/Fe_3O_4(001)$  model catalyst.

## 4.1. Adsorption and incorporation

The STM image and structural model of the bare  $Fe_3O_4(001)$  adsorption template are shown in Fig. 4.2(a). The bright protrusions in the STM image represent the octahedrally coordinated iron atoms  $Fe_{oct}$ . They are usually seen in STM images just as bright undulating rows which run in the <110> direction over the surface. Surface oxygen atoms (O<sub>s</sub>) are not imaged because they have zero density of states in the vicinity of the Fermi energy [73]. The ability of (001) surface to successfully support and stabilize metal adatoms is linked to the ( $\sqrt{2} \times \sqrt{2}$ )R45° surface reconstruction. The reconstructed (001)

#### 4.1. ADSORPTION AND INCORPORATION

surface can accommodate metal adatoms only in sites where a tetrahedrally coordinated iron atom Fe<sub>tet</sub> is missing in the subsurface layer, i.e., narrow sites (green cross in Fig. 4.2(a)). Therefore, the reconstructed  $Fe_3O_4(001)$  surface can only accommodate 1 metal adatom per surface unit cell, which is consistent with previous results in case of other metals, e.g., Au, Ag, Pt, Pd [49–52]. In this study the same behaviour was observed for Rh adatoms, but the STM measurements revealed the presence of two types of Rh adatoms on the surface. Both are adsorbed in narrow sites, but their apparent shape and height are different. The apparent height of the majority of adatoms (called regular adatoms  $Rh_1^{reg}$  – Fig. 4.2(b)) varies with the bias voltage from ~100 pm at +2.5 V to  $\sim$ 185 pm at +1.1 V. Most of the STM images presented in this study were acquired at +1.6 V. The apparent height at these conditions is  $\sim 150$  pm, while the apparent height of the small fraction of Rh adatoms (called low adatoms  $Rh_1^{low}$  – the adatoms in red circles in Fig. 4.3(a)) is only  $\sim 125 \text{ pm}$  at +1.6 V bias voltage. The ratio of coverage of Rh<sub>1</sub><sup>low</sup> to coverage of  $Rh_1^{reg}$  adatoms varies a lot depending on the base pressure condition from 0.17 up to 0.4. However, these lower  $Rh_1^{low}$  adatoms become regular ones after scanning the area at high bias voltage (+3 V). This phenomenon is shown in Fig. 4.3(b). In general, both types of Rh adatoms are stable and immobile at room temperature.



Figure 4.2: STM images and corresponding structural models of: (a) the bare  $Fe_3O_4(001)$  and (b) rhodium adatom adsorbed on  $Fe_3O_4(001)$  surface. In structural models the  $Fe_{oct}$  atoms are coloured in dark blue,  $Fe_{tet}$  in light blue, O atoms in red and Rh in green.

In contrast to what has been observed for the other metals, Rh adsorbs on magnetite(001) surface not only in adatom phase, but also as  $Rh_2^{osc}$  dimers. They can be easily distinguished from adatoms due to their oval shape. Their apparent height is similar to the height of adatoms, i.e., ~160 pm at bias voltage +1.6 V.  $Rh_2^{osc}$  dimers are also situated in narrow sites, but they undergo oscillation around narrow site in the row direction. Basically, one atom of a  $Rh_2^{osc}$  dimer is always situated in a narrow site. The another one is closer to the wide site in the <110> direction or the opposite one.

In Fig. 4.4 two consecutive images from the STM movie show the oscillation of a  $Rh_2^{osc}$  dimer. The nodes of the grid mark the positions of narrow sites. The dimer is marked by

## 4. $RH/FE_3O_4(001)$ MODEL CATALYST



Figure 4.3: Two images selected from an STM movie acquired over the same sample area. (a) Lower  $Rh_1^{low}$  adatoms are marked by red circles. (b) After scanning this whole area at +3 V the atoms in red circles have the usual apparent height of regular  $Rh_1^{reg}$  adatoms.

a red circle. DFT calculations are needed to unravel the mechanism of this oscillation. Unfortunately, none were done, therefore we can only propose two possible ways how this oscillation might work. Firstly, the Rh atom closer to the wide site moves around or above the atom situated firmly in a narrow site. The second possibility is that this atom moves into the narrow site and the other one moves out of it.



Figure 4.4: Two consecutive STM images from a movie showing two configurations of a  $Rh_2^{osc}$  dimer (red circle). The nodes of the grid mark the narrow sites. Yellow circle is just the middle of the grid placed in a narrow site.

The profile of a dimer (see Fig. 4.5) is not symmetrical. The part of a dimer situated in a narrow site is slightly lower than the another one and the part closer to the wide site is steeper. The profile has this shape regardless the bias voltage, row orientation and experimental day. We tried to break the dimer by scanning at high bias voltage. We were able to break two dimers. One dimer split into two adatoms after scanning the whole image at the bias voltage +3 V (Fig. 4.6). The second dimer split only into 1 adatom. The another atom was probably attached to the tip. We were unable to reproduce the dimer splitting, so it might have been a spontaneous process.

Moreover, there are present some defects of the surface reconstruction. Most common are surface hydroxyl ( $O_sH$ ) groups (see Fig. 4.3 – cyan rectangles), formed through the reaction of water and oxygen vacancies during the sample preparation [74]. They modify the density of states of the neighbouring Fe<sub>oct</sub> atoms, making them appear brighter in STM images [47].

As mentioned in section 3.2 the water cooled QCM was used for calibration of the deposition rate. After depositing  $0.2 \,\mathrm{ML}$  Rh on magnetite(001) we got a real cover-

## 4.1. ADSORPTION AND INCORPORATION



Figure 4.5: Profile of a  $Rh_2^{osc}$  dimer scanned at +1.6 V. Red vertical line marks the position of a narrow site. This profile is measured along the row direction exactly between the Fe<sub>oct</sub> rows.



Figure 4.6: Consecutive STM images from a movie measured in UHV showing a dimer splitting into two adatoms after scanning at +3 V.

age (calculated from STM images) for adatoms approximately 0.13 ML and for dimers 0.0069 ML. In case of 0.5 ML, we got the real coverage 0.31 ML for adatoms and 0.0186 ML for dimers. This difference between the calibrated coverage and real one is quite significant. We have only 60 - 70% of the calibrated coverage.

There are two possible reasons why the real coverage does not correspond with the calibrated one. Firstly, it is possible that QCM measurement is wrong. This was rejected, because in case of other metals (Ir, Cu) we got approximately the same real coverage as the calibrated one. The second possibility is that Rh atoms go into the subsurface or bulk even at room temperature. Therefore, we heated the sample to find the appearance of Rh atoms embedded into the subsurface in STM images and afterwards tried to find whether these structures are present on the surface even without heating. The result of this experiment is shown in Fig. 4.7. The coverage of adatoms decreased from 0.14 ML to 0.016 ML and dimers disappeared completely after heating the sample to 250 °C. On the other hand, many bright features looking similar to surface hydroxyl groups appeared. Fortunately,  $O_sH$  groups exhibit a characteristic hopping between two surface oxygen atoms [74], thus we could easily distinguished them from these new features that appeared after heating. After further heating to 320 °C (Fig. 4.7(b)) no change was observed.

To completely understand the incorporation of rhodium, we need to get back to the structural model of  $(\sqrt{2} \times \sqrt{2})$ R45° surface reconstruction (Fig. 4.8). There are 3 possible candidate sites for incorporation of rhodium atoms into the surface: the surface octahedral site Fe<sub>oct</sub>(S) (so called Rh<sub>oct</sub>(S) configuration), a tetrahedral site in the first subsurface layer Fe<sub>tet</sub>(S-1) (Rh<sub>tet</sub>(S-1) configuration) and an octahedral site in the second subsurface



Figure 4.7: STM images of 0.2 ML Rh on magnetite (001) heated to: (a) 250 °C and (b) 320 °C. OH groups are marked by a cyan square.

layer Fe<sub>oct</sub>(S-2) (Rh<sub>oct</sub>(S-2) configuration). In the first two configurations two Fe vacancies in the S-2 layer are filled by Fe<sub>int</sub> atom and one Fe<sub>oct</sub>(S) atom. In the last configuration they are filled by Fe<sub>int</sub> atom and one Rh atom. This occupation of the cation sites corresponds to a bulk-terminated Fe<sub>3</sub>O<sub>4</sub>(001) surface with one Fe substituted by Rh. Unfortunately, no DFT calculations were done for this system yet, so we can only estimate from the results for Ti incorporation in Fe<sub>3</sub>O<sub>4</sub>(001) [75].



Figure 4.8: DFT+U-optimized structural model of the  $(\sqrt{2} \times \sqrt{2})$ R45°-Fe<sub>3</sub>O<sub>4</sub>(001) surface. The black triangle indicates the region where the subsurface differs from the regular spinel structure. Two octahedral Fe atoms are missing from the subsurface Fe<sub>oct</sub>-O layer (S-2) beneath Fe<sub>int</sub>(dashed blue circles).

DFT calculations showed that the  $Ti_{tet}(S-1)$  geometry is unfavourable configuration.  $Ti_{oct}(S)$  and  $Ti_{oct}(S-2)$  geometries are approximately equivalent, but the  $Ti_{oct}(S-2)$  is slightly more favourable. Measured STM images as well as calculated ones of these two configurations correspond with the measured STM images of Rh after heating, therefore we can assume that rhodium incorporates in the same configurations as Ti. The STM images with the most probable structural models of Rh atoms incorporated in the magnetite(001) surface are shown in the Fig. 4.9.

## 4.2. WATER DISSOCIATION



Figure 4.9: STM images with the most probable structural models of Rh atoms incorporated in the magnetite(001) surface: (a)  $Rh_{oct}(S)$  configuration and (a)  $Rh_{oct}(S-2)$  configuration.

 $Rh_{oct}(S)$  configuration (see Fig. 4.9(a)) looks in STM like one bright spot in a Fe<sub>oct</sub> row. Basically, the Rh atom goes into the outermost surface layer instead of one  $Fe_{oct}(S)$ atom, which fills the cation vacancy  $V_{Fe}$  directly below (vacancy  $V_{Fe}$  is shown in Fig. 4.8). The other cation vacancy is filled by Fe<sub>int</sub> atom. These features are situated in STM images only in wide sites above the cation vacancies  $V_{Fe}$  and that is in an agreement with our hypothetical structural model. The  $Rh_{oct}(S-2)$  configuration (see Fig. 4.9(b)) looks like two  $O_sH$  groups next to each other situated in a wide site. In this case, the subsurface cation vacancies are filled by one Rh atom and one Fe<sub>int</sub> atom. In both configurations, the filling of subsurface cation vacancy with Rh or Fe<sub>oct</sub> atom induces Fe<sub>int</sub> to occupy the other vacancy. From the difference in the coverage of  $Rh_{oct}(S-2)$  and  $Rh_{oct}(S)$  species (0.05 ML and 0.016 ML, respectively) we can say that  $\text{Rh}_{\text{oct}}(\text{S-2})$  configuration is more favourable. Now, we should return to the original task and that is to find out if these species are present on the surface even without heating. We found out that  $Rh_{oct}(S-2)$ species really are there, but their coverage is very low (only 0.002 ML). This amount does not balance the difference between the calibrated and real coverage of Rh atoms, therefore we conclude that the missing atoms diffused into the bulk.

## 4.2. Water dissociation

The studied system is highly active in water adsorption. The initial (a) and the final (b) states after the exposure of  $Rh_1/Fe_3O_4(001)$  model catalyst to 1 L of water are shown in Fig. 4.10. There are two trends we observed upon water dosing. First, the coverage of surface hydroxyls  $O_sH$  has increased from 0.075 ML up to 0.164 ML. Second, the coverage of  $Rh_1^{low}$  adatoms has also been increased from 0.0153 ML to 0.038 ML, while the coverage

### 4. $RH/FE_3O_4(001)$ MODEL CATALYST

of  $Rh_1^{reg}$  decreased from 0.069 ML to 0.056 ML. The change in the amount of surface hydroxyl groups is associated with the dissociative adsorption of water [74]. The water molecule is split into into a hydroxyl group  $O_wH$  (the subscript "w" informs about the origin of the hydroxyl group, i.e., water molecule) and hydrogen atom H upon adsorption. The hydrogen atom is highly reactive and binds to the surface oxygen, i.e., the  $O_sH$  is formed. The  $O_wH$  can either form the  $H_2O$  molecule with another  $O_wH$  and desorb afterwards, or more probably bind to the  $Rh_1$  adatom. The adsorption of the hydroxyl group from the water molecule ( $O_wH$ ) on  $Rh_1$  adatom changes the adatom's electronic state, therefore its apparent morphology observed in STM is different. This is observed in the STM as the increment in the coverage of  $Rh_1^{low}$  adatoms, and the decrement in the coverage of  $Rh_1^{reg}$  into  $Rh_1^{reg}$  adatoms after the adsorption of  $O_wH$  on  $Rh_1^{reg}$ . From this it is clear, that so called  $Rh_1^{low}$  adatoms probably are  $Rh_1-O_wH$  hydroxyls.

There is another experiment that confirms the hypothesis of  $Rh_1^{low}$  adatoms being  $Rh_1-O_wH$  hydroxyls. In section 4.1 (see Fig. 4.3) we showed the possibility of the transformation of  $Rh_1^{low}$  back into the  $Rh_1^{reg}$  adatoms upon scanning at high bias voltage. Because there are many studies about the desorption of adsorbed gas molecules induced by scanning at high bias voltages [76,77], the transformation observed in this experiment could be the desorption of a molecule from the Rh adatom. From the STM measurements upon the exposure of studied model catalyst to water we think that this molecule probably is  $O_wH$  hydroxyl.

There are several  $Rh_{oct}(S-2)$  species (see Fig. 4.9) on the surface in Fig. 4.10(b). Their apparent morphology is similar to the appearance of two  $O_sH$  next to each other, which makes the calculation of the coverage of surface hydroxyls quite challenging. Fortunately, using STM movies we were able to distinguish between these two species thanks to the fact, that  $O_sH$  hop over the surface at room temperature while  $Rh_{oct}(S-2)$  species are immobile.



Figure 4.10: Water splitting at the Rh/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst. (a) The initial state of Rh/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst. The coverages of O<sub>s</sub>H and Rh<sub>1</sub>–O<sub>w</sub>H (Rh<sub>1</sub><sup>low</sup>) are 0.075 ML and 0.0153 ML, respectively. (b) The system after dosing 1 L of water. The coverages of O<sub>s</sub>H and Rh<sub>1</sub>–O<sub>w</sub>H (Rh<sub>1</sub><sup>low</sup>) increased to 0.164 ML and 0.038 ML, respectively.

## 4.2. WATER DISSOCIATION

It is well known that  $Fe_3O_4(001)$  surface can split water at room temperature on its own. However, the rate is much lower. The coverage of  $O_sH$  hydroxyls changed from 0.064 ML to 0.117 ML after dosing 4.5 L of water on clean  $Fe_3O_4(001)$  surface (see Fig. 4.11). We got slightly higher coverage of  $O_sH$  after the exposure to 4.5 times smaller amount of water when the Rh was present on the surface. Therefore, our results show that the Rh species present on  $Fe_3O_4(001)$  markedly assist in water dissociation.



Figure 4.11: (a) The STM image of a clean magnetite (001) surface. Two surface hydroxyls  $\rm O_sH$  are highlighted by yellow half circles. Their coverage is 0.064 ML. (b) The STM image of a magnetite (001) surface after dosing 4.5 L of water. The coverage of  $\rm O_sH$  increased to 0.117 ML. Images are not acquired over the same sample area.

## 4.3. CO adsorption

 $Rh_2^{osc}$  dimers were found to be active in CO adsorption. The CO adsorption was already observed while the sample was kept in a background pressure of  $7 \times 10^{-11}$  mbar. At this point, it was still unclear, if it really is CO or some other background gas. Therefore, we acquired several STM movies while the background CO pressure was purposely raised to  $2-5 \times 10^{-10}$  mbar. Every movie showed that  $Rh_1$  adatoms are inactive regarding CO and no transformation of  $Rh_1^{reg}$  into  $Rh_1^{low}$  or  $Rh_1^{low}$  into  $Rh_1^{reg}$  adatoms was observed. In these movies only  $Rh_2^{osc}$  dimers could adsorb CO molecules. The Fig. 4.12 shows 2 consecutive frames of a STM movie recorded in  $p_{CO}=2\times 10^{-10}$  mbar. In the center of Fig. 4.12(a) the  $Rh_2^{osc}$  dimer (red circle) is situated in a narrow site with an apparent height ~160 pm, but then in Fig. 4.12(b) is replaced by a bright fuzzy feature with apparent height ~300 pm. The dimer does not undergo typical oscillation after the CO molecule adsorption.



Figure 4.12: 2 consecutive frames of a STM movie recorded in  $p_{\rm CO}=2\times10^{-10}$  mbar. (a) Rh<sub>2</sub> dimer without adsorbed CO molecule. (b) Rh<sub>2</sub><sup>osc</sup>-CO carbonyl appears in STM as a bright fuzzy protrusion.

DFT calculations would be necessary to find out the structural model of a  $Rh_2^{osc}$ -CO carbonyl. The very interesting phenomenon is that  $Rh_1^{reg}$  adatoms are inactive in CO molecule adsorption. Nevertheless, we expect that for  $Rh_2^{osc}$  we will find out the *d*-band center significantly shifted to higher energy than for  $Rh_1^{reg}$  adatoms. The reason for this hypothesis is that theoretic calculations show that catalysts with more empty *d* states interact stronger with CO [78].

The appearance of  $Rh_2^{osc}$ -CO in STM is similar to that of Pd<sub>2</sub>-CO [52]. Therefore we expect that the structural model will be based on a CO molecule oriented almost vertically to the surface. The fuzzy appearance of  $Rh_2^{osc}$ -CO carbonyl in STM images is because of bending of CO molecule sticking from the surface by the STM tip while scanning.

However,  $Rh_2^{osc}$ -CO and  $Pd_2$ -CO carbonyls behave differently. Both structures are immobile, but only  $Rh_2^{osc}$ -CO is stable. It was observed that  $Pd_1$ -CO carbonyl can detach from a  $Pd_2$ -CO complex and jump to another place leaving  $Pd_1$  adatom in the former position. This behaviour is determined by the interplay between the strength of the bonding of metal atoms forming a dimer to the substrate and between them and weakening of these bonds upon the CO molecule adsorption. The stronger the bond between metal atom and CO molecule is, the weaker the bond between metal atoms and their bonding to the substrate becomes. This weakening can be estimated from the adsorption energy of CO on Pd(111) and Rh(111). These energies are 1–1.2 eV on Pd(111) [79] and 1.65 eV on Rh(111) [80] (for top site). The bond between Rh atoms should be more weakened

## 4.3. CO ADSORPTION

than between Pd atoms (approximately by 0.5 eV). But we observed the opposite. This is due to the very strong bond between the Rh atoms forming a dimer. This strength can be estimated from cohesive energies. Cohesive energy of Pd is  $E_{\rm coh}^{\rm Pd} = 3.89 \,{\rm eV}/{\rm atom}$ , for Rh it is  $E_{\rm coh}^{\rm Rh} = 5.75 \,{\rm eV}/{\rm atom}$  [81]. So clearly, Rh<sub>2</sub><sup>osc</sup> should be much more stable than Pd<sub>2</sub> dimer.

The example of the STM movie acquired over the same sample area in the background CO pressure  $p_{\rm CO} = 2 \times 10^{-10}$  mbar is shown in Fig. 4.13. After the dose of 1.25 L of CO all Rh<sub>2</sub><sup>osc</sup> adsorbed CO molecule and formed Rh<sub>2</sub><sup>osc</sup>-CO carbonyls.



Figure 4.13: STM movie acquired in the background CO pressure  $p_{\rm CO}=2\times10^{-10}$  mbar. (a) All Rh<sub>2</sub> dimers in this sample area are marked by cyan circles. (b) Dimer in a red circle moved (typical oscillation). (c) Adsorption of CO molecule on a Rh<sub>2</sub> dimer (yellow circle) and another dimer moved. (d) The same dimer moved. (e) That dimer moved again and CO adsorbed on a different one. (f) CO molecule was adsorbed on the last free dimer in the scanned area.

Our model catalyst shows high reactivity in respect to water and CO adsorption. This is a key prerequisite for the application of this system as a potential water gas shift (WGS) catalyst. Water gas shift (see Eq. 4.1) is important reaction to produce hydrogen for chemical processing and to remove CO contamination in feed streams for ammonia synthesis and fuel cells [82].

$$CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2(g)} + H_{2(g)}$$

$$(4.1)$$

However, there are open issues that should be addressed before it will be possible to use it in real systems. Most importantly it is necessary to increase the coverage of active sites for CO adsorption. The  $Rh_2^{osc}$  dimers are formed during deposition when Rh atom lands on another one, therefore the deposition of higher amounts of Rh might be a possible way. Unfortunately, this experiment was not carried out.

## 4.4. Oxygen induced adatom sintering

Nowadays, it is well known that sintering (agglomeration of atoms into the clusters) is primarily thermally driven, but the coarsening of catalytically active metal clusters can also be accelerated by the presence of gases [83]. It was reported that Pd and Pt on Fe<sub>3</sub>O<sub>4</sub>(001) sinter in the presence of CO [51, 52]. On the other hand, O<sub>2</sub> adsorption induces sintering of Rh on Fe<sub>3</sub>O<sub>4</sub>(001) (Fig. 4.14). Of course, this process is undesirable in the study of the catalytic performance of single atom catalysts. Nevertheless, it is very important to identify the key processes that underlie gas-induced mass transport at surfaces.



Figure 4.14: Interaction of Rh/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst with O<sub>2</sub>. (a) Initial state of a Rh/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst. The Rh<sub>2</sub><sup>osc</sup> dimers are highlighted by green circles (b) Partially (adatoms are still present) sintered Rh after dosing 1.125 L of O<sub>2</sub> on the sample. Not all clusters consisting of the same amount of atoms look the same. Clusters consisting of one Rh<sub>1</sub>–O<sub>w</sub>H (Rh<sub>1</sub><sup>low</sup>) are highlighted by cyan colour and the white ones are formed only by regular Rh adatoms. Both images were acquired by STM at room temperature over the same surface area.

In comparison with CO adsorption, no change is observed in the apparent height upon  $O_2$  adsorption only the transport of metal adatoms at the surface. The atomically resolved STM movies allowed us to follow the evolution from well-dispersed Rh adatoms into clusters step-by-step. Only Rh<sub>1</sub><sup>reg</sup> adatoms were moving over the surface in these movies. All other Rh species, i.e., Rh<sub>1</sub>–O<sub>w</sub>H (or Rh<sub>1</sub><sup>low</sup>), Rh<sub>2</sub><sup>osc</sup>, and clusters, were immobile, except for the oscillation of Rh<sub>2</sub><sup>reg</sup> adatoms. Each cluster was formed when one or more Rh<sub>1</sub><sup>reg</sup> jumped on another adatom. Obviously, Rh<sub>1</sub>–O<sub>w</sub>H is immobile, because it cannot adsorb  $O_2$  molecule when there is already adsorbed hydroxyl O<sub>w</sub>H. The reason why clusters are immobile is unclear. There are two possibilities. First, the O<sub>2</sub> molecule is desorbed after the cluster formation, so the bonding to the substrate is strengthened. Second, the O<sub>2</sub> stays adsorbed on a cluster, but the bonding to the substrate is not weakened enough for the whole cluster to diffuse over the surface. All clusters are situated in a narrow site, because in every cluster formation event one or more Rh<sub>1</sub><sup>reg</sup> jumped on another Rh adatom situated in a narrow site and they are immobile. Therefore, only small clusters

#### 4.4. OXYGEN INDUCED ADATOM SINTERING

can be formed if the adatom coverage is low enough as  $Rh_1^{reg}$  adatom can jump maximally  $\sim 4 \,\mathrm{nm}$ .

The formation of  $Rh_2$  dimer consisting of two  $Rh_1^{reg}$  adatoms by sintering is shown in Fig. 4.15(a). These dimers appear differently from  $Rh_2^{osc}$  dimers in STM (see Fig. 4.15(b)) and do not exhibit oscillation. Interestingly, the cluster formation was never recorded by an STM movie. In most cases, the  $Rh_1^{reg}$  adatoms were separated by some distance in one frame and in the next (time difference of roughly 4 min) the cluster was already formed. This could be the effect of STM tip that prevents the movement of  $Rh_1^{reg}$  with adsorbed  $O_2$  molecule or the tip even prevents the adsorption of  $O_2$  molecule itself. In all movies we were able to capture the movement of  $Rh_1^{reg}$  adatoms over the surface only twice (see Fig. 4.15(c)).



Figure 4.15: Oxygen adsorption induced sintering of Rh species on  $Fe_3O_4(001)$  surface. (a) The formation of Rh<sub>2</sub> dimer consisting of two Rh<sub>1</sub><sup>reg</sup> adatoms. (b) The detail on Rh<sub>2</sub><sup>osc</sup> dimer. (c) The hopping of a Rh<sub>1</sub><sup>reg</sup> adatom upon adsorption O<sub>2</sub>.

The adsorption of  $O_2$  molecule on single metal atoms supported by metal oxides was theoretically studied very thoroughly in recent years [78, 84–86]. In these studies it was

#### 4. $RH/FE_3O_4(001)$ MODEL CATALYST

found out that  $O_2$  molecule is preferably adsorbed on a surface oxygen vacancy in the vicinity of metal atom supported by reducible iron oxide (FeO<sub>x</sub>). The adsorption energy on oxygen defective Rh<sub>1</sub>/FeO<sub>x</sub> is 1.82 eV. For oxygen adsorption on vacancy-free Rh<sub>1</sub>/FeO<sub>x</sub> is in the best configuration  $O_2$  molecule parallel to the substrate with the adsorption energy 0.79 eV [78]. This makes Rh the most reactive metal (among the investigated ones) in oxygen adsorption. Therefore, the weakening of the bond of Rh<sub>1</sub><sup>reg</sup> adatom to the subtrate is very strong which results in sintering of Rh adatoms.

We tried to use the sintering of Rh adatoms in oxygen atmosphere to increase the coverage of active sites for CO adsorption, i.e.,  $Rh_2$  dimers and consecutively, use this system for water gas shift reaction (see Eq. 4.1). Unfortunately, dimers formed by sintering are unreactive in CO adsorption, therefore not usable in water gas shift catalysis.

However, we have a system strongly interacting with  $O_2$  molecules and also active in CO adsorption. Therefore, we investigated its potential in the catalytic oxidation of carbon monoxide (see Eq. 4.2). This reaction has application in CO removal from car exhausts [87] and has become a classical textbook example of heterogeneous catalysis. This reaction is well studied because of its simplicity.

$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$$
 (4.2)

In [78] the existence of OOCO<sup>\*</sup> intermediate was proposed (see Fig. 4.16), when both CO and  $O_2$  are adsorbed on a metal atom. We tried few experiments, when we firstly adsorbed CO on Rh<sub>2</sub><sup>osc</sup> dimers and then dosed  $O_2$  on the surface. This intermediate was not observed, just few adsorbed CO molecules disappeared. This might mean that  $O_2$  molecule interacted with CO and CO<sub>2</sub> molecule was formed. These experiments are unconvincing because desorption of CO molecules could be caused by the influence of the scanning tip and moreover, desorption of CO was observed in some cases even without dosing  $O_2$ . Furthermore, we would need a lot more Rh<sub>2</sub><sup>osc</sup>-CO carbonyls to prove this statistically.



Figure 4.16: OOCO<sup>\*</sup> intermediate in Langmuir-Hinshelwood mechanism of CO oxidation on vacancy free  $Rh_1/FeO_x$  which is formed after the  $O_2$  and CO coadsorption. The picture was taken from [78].

## 4.5. NO adsorption induced diffusion

Our experiments confirmed that  $Rh/Fe_3O_4(001)$  is very active in NO adsorption. The apparent morphology of  $Rh_1^{reg}$  adatoms and  $Rh_2^{osc}$  dimers changes upon adsorption of NO molecule (see Fig. 4.17).



Figure 4.17: STM images of: (a)  $Rh_1^{reg}$  adatom, (b) NO molecule adsorbed on  $Rh_1^{reg}$  adatom, (c)  $Rh_2^{osc}$  dimer and (d) NO molecule adsorbed on a dimer. Images are not acquired over the same surface area.

 $Rh_1^{reg}$  adatoms have apparent height ~150 pm. After the NO adsorption, the apparent height is ~250 pm. The apparent height of  $Rh_2^{osc}$  dimers is ~155 pm. After NO adsorption it is increased to ~260 pm, which is by 40 pm less, then for Rh carbonyl species. The profile of a  $Rh_2^{osc}$ -NO nitrosyl is similar to the profile of  $Rh_2^{osc}$  dimer without adsorbed NO molecule (see Fig. 4.5). The part of a dimer situated in a narrow site is still lower than the another, only the difference is more significant (~8 pm). In [88] the structural model of NO adsorbed on Co<sub>1</sub> adatom anchored on graphene was determined by DFT calculations. NO molecule binds to Co adatoms by N atom and the whole molecule is nearly vertical to the support surface. We can expect the structural model for NO adsorbed on Rh<sub>1</sub> adatoms supported by magnetite(001) will be similar. In contrast to Pd<sub>1</sub>-CO and Rh<sub>2</sub><sup>osc</sup>-CO carbonyls, we did not observe any scratchiness indicating the interaction of molecule sticking perpendicularly from the surface with the STM tip.

In contrast to previous studied gases (CO and  $O_2$ ), NO molecules can not go under the tip. Therefore, we were unable to record STM movies capturing the adsorption process.

#### 4. $RH/FE_3O_4(001)$ MODEL CATALYST

Firstly, we dosed 0.85 L of NO on Rh/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst and then acquired STM movie. In Fig. 4.18 is shown first and last image of a 2 hours long STM movie acquired over the same sample area. This dose was sufficient enough for all Rh<sub>1</sub><sup>reg</sup> adatoms and Rh<sub>2</sub><sup>osc</sup> dimers to adsorb NO molecule. The species that were observed on the surface without adsorbed NO molecule are Rh<sub>1</sub><sup>low</sup> adatoms (see Fig. 4.18(a), red circles). This is in a good agreement with our hypothesis that these species actually are Rh<sub>1</sub><sup>reg</sup>–O<sub>w</sub>H hydroxyls, therefore they can not adsorb NO molecules. From the nature of this experiment it is unclear whether some Rh<sub>1</sub><sup>low</sup> adatoms adsorbed NO or not, because we could not scan the same sample area before and after NO dosing.

The STM movie showed that upon NO adsorption  $Rh_1$ –NO nitrosyls become mobile and diffuse over the surface but almost without sintering. The coverage of  $Rh_1^{reg}$ –NO nitrosyls in Fig. 4.18(a) is 0.106 ML, but after two hours their coverage decreased to 0.064 ML.



Figure 4.18: First (a) and last (b) images from a STM movie recorded after NO adsorption on Rh species. Images were acquired over the same surface area. In (a) green circles highlight dimers with adsorbed NO molecules and red ones  $Rh_1^{low}$  adatoms, i.e.,  $Rh_1^{reg}$ –  $O_wH$ . The green dashed circles in (b) highlight dimers formed by sintering.

The Fig. 4.19 shows all events observed in a STM movie after NO adsorption on Rh species. In the first 4 images (a-d) of Fig. 4.19 are shown the possible ways of diffusion over the surface. The mobile species are  $Rh_1^{reg}$ -NO nitrosyls. The movement of a dimer was seen only once and tetramers are completely immobile. In average, 11 % of  $Rh_1^{reg}$ -NO nitrosyls move in each frame of a STM movie and 12 % of these movements lead to the cluster formation. The most common movement is a jump by one surface unit cell (on a narrow site) in a row direction (Fig. 4.19(a)), but  $Rh_1^{reg}$ -NO can also move by two unit cells in row direction (Fig. 4.19(b)). Less common is the jump between the rows on a neighbour narrow site (Fig. 4.19(c)) and the jump over the dimer is very scarce (Fig. 4.19(d)). Note that in this case, it is possible that the  $Rh_1^{reg}$ -NO nitrosyl jumped on a  $Rh_2$ -NO dimer, formed a trimer, which split again into a dimer and one  $Rh_1^{reg}$ -NO nitrosyl on the other side of a dimer.

In Fig. 4.19(e) a  $Rh_2$ -NO dimer is formed when two  $Rh_1^{reg}$ -NO meet. Usually one  $Rh_1^{reg}$ -NO jumps on another one, but sometimes two  $Rh_1^{reg}$ -NO can jump on the same place, where the cluster is formed. Fig. 4.19(f) shows the formation of an unstable trimer. All trimers that were formed, split back into the  $Rh_1^{reg}$ -NO nitrosyl and a  $Rh_2$ -NO dimer in the next image (see Fig. 4.19(h)), the same trimer). In Fig. 4.19(h) a tetramer

## 4.5. NO ADSORPTION INDUCED DIFFUSION

was formed, when two  $Rh_1^{reg}$ -NO jumped on a  $Rh_2$ -NO dimer. In contrast to trimers, tetramers are stable.



Figure 4.19: Events observed in a STM movie after dosing 0.85 L of NO on Rh/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst. (a) Rh<sub>1</sub><sup>reg</sup> moves by one surface unit cell in a row direction, (B) Rh<sub>1</sub><sup>reg</sup>-NO moves by 2 surface unit cells in a row direction, (c) Rh<sub>1</sub><sup>reg</sup>-NO jumps between the rows, (d) Rh<sub>1</sub><sup>reg</sup>-NO jumps over Rh<sub>2</sub>-NO, (e) Rh<sub>2</sub>-NO dimer formation, (f) Rh<sub>3</sub>-NO trimer formation, (g) Rh<sub>4</sub>-NO tetramer formation, (h) Splitting of a Rh<sub>3</sub>-NO trimer.

# 5. $Ir/Fe_3O_4(001)$ model catalyst

This chapter is dedicated to the second studied model catalyst:  $Ir/Fe_3O_4(001)$ . The performance of this catalyst was studied in the same way as  $Rh/Fe_3O_4(001)$  model catalyst in the previous chapter. Rhodium and iridium are both metals from the same column in the periodic table of elements. Therefore, we could expect that their behaviour in the interaction with gases will be similar. Our experiments proved this, but the interaction of  $Ir/Fe_3O_4(001)$  model catalyst with gas molecules is weaker than in case of  $Rh/Fe_3O_4(001)$ . The presence of Ir species on the surface was confirmed by XPS. The measured Ir 4f peak is shown in Fig. 5.1. The peak Ir  $4f_{7/2}$  has approximately the same position as the peak for metallic iridium (60.9 eV – red vertical line in XPS spectrum).



Figure 5.1: The Ir 4f peak of  $Ir_1/Fe_3O_4(001)$  model catalyst.

We found out that magnetite(001) surface can accommodate  $Ir_1$  adatoms (see Fig. 5.2(a), green circle) and  $Ir_2$  dimers (Fig. 5.2(a), cyan circle).  $Ir_2$  dimers are different from  $Rh_2^{osc}$  dimers.  $Ir_2$  dimers are immobile and they do not show any oscillations. They are not symmetric, one part of a dimer is higher by ~40 pm than the other. The proposed model of  $Ir_2$  (not based on DFT calculations, just illustrative one) is shown in Fig. 5.2(b). There is one additional structure on the surface observed after deposition of Ir at room temperature. This structure looks like an adatom but is scratchy (Fig. 5.2(a) red circle). Similarly to the Rh, this might be  $Ir_1$  adatom that adsorbed some gas molecule from the background. Unfortunately, we were unable to find the identity of this gas. After deposition of calibrated 0.3 ML of Ir, the coverage for adatoms was 0.193 ML, for dimers 0.084 ML and for scratchy structures only 0.006 ML. Total coverage is then 0.283 ML, which is almost what it should be. Hence, we conclude that Ir atoms do not incorporate in the magnetite surface so easily as Rh atoms. There could be more reasons, but the most probable one is that Ir atoms are simply bigger than Rh atoms.

Ir on magnetite(001) is stable up to 300 °C. The majority of adatoms is incorporated into the surface after heating. Initially, the adatom coverage was 0.09 ML, but after heating it decreased to 0.005 ML. The STM image of Ir/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst after heating to 300 °C is shown in Fig. 5.3. This image captures all structures present on the surface after heating, except for very scarce clusters. The Ir adatom that stayed on the surface is highlighted by a yellow circle. The incorporation of Ir is based on the same



Figure 5.2: (a) STM image of Ir species on  $Fe_3O_4(001)$  surface. The Ir<sub>1</sub> adatom is highlighted by a green circle, the Ir<sub>2</sub> dimer is in a cyan circle and the scratchy structure is in a red circle. (b) Proposed structural model of a Ir<sub>2</sub> dimer. Ir atoms are silver. The yellow cross marks the narrow site (usual adsorption site).

fundamental principles as incorporation of Rh. 2 configurations were also observed for Ir. Firstly, Ir is incorporated in  $Ir_{oct}(S)$  configuration (see Fig. 5.3, green circle) and secondly in  $Ir_{oct}(S-2)$  configuration (Fig. 5.3, red circle). These configurations are described in section 4.1. No dimers were observed in STM images after heating. It is possible that the resolution was not good enough and we mistook them for clusters or they split upon heating. It appears that  $Ir_{oct}(S)$  configuration is more favourable than  $Ir_{oct}(S-2)$ , because their coverages are 0.05 ML and 0.02 ML, respectively. On the other hand, Rh favoured more the  $Rh_{oct}(S-2)$  configuration.



Figure 5.3: The STM image of Ir on magnetite(001) heated to 300 °C. The Ir adatoms are incorporated in a surface in two configurations:  $Ir_{oct}(S)$  – green circle and  $Ir_{oct}(S-2)$  – red circle. Few adatoms stayed on the surface – yellow circle.

#### 5. $IR/FE_3O_4(001)$ MODEL CATALYST

Ir<sub>1</sub>/Fe<sub>3</sub>O<sub>4</sub> is a very stable system. In STM movie acquired in UHV no changes were observe, just each frame looked the same as the previous one. Moreover, this system interacts with gas molecules very weakly. The adsorption of CO was not observed. Ir sinters in O<sub>2</sub> atmosphere like Rh, but this effect is much weaker. Fig. 5.4(a) shows the initial state of the surface (adatom coverage is 0.137 ML) and in Fig. 5.4(b) is the STM image of this surface after dosing 20 L of O<sub>2</sub> (not the same surface area). Clearly, there is still plenty of Ir<sub>1</sub> adatoms. Their coverage decreased only to 0.083 ML. We did not record the STM movie, because it would take many hours to see any sintering at the pressures we can use in the chamber. Ir<sub>1</sub> adatoms can adsorb NO molecules. They look in STM similarly to Rh–NO nitrosyls, but Ir–NO nitrosyls have lower apparent height ~210 pm. The diffusion rate of Ir<sub>1</sub>–NO nitrosyls is very low. Dimers were not observed in STM images after dosing NO. They might split after the NO adsorption like Rh<sub>3</sub>–NO trimers.



Figure 5.4: (a) The initial state of  $Ir/Fe_3O_4(001)$  model catalyst. (b) The STM image after dosing 20 L of  $O_2$  on this system. Images are not acquired over the same sample area.

6.  $CU/FE_3O_4(001)$  MODEL CATALYST

# 6. $Cu/Fe_3O_4(001)$ model catalyst

The last studied metal deposited on magnetite (001) surface is copper. Similarly to other metals, copper also is in an adatom phase. But in comparison with other metals, copper adatoms are situated in two sites and we did not observe any dimers. Firstly, there are regular  $Cu_1^{reg}$  adatoms situated in a narrow site (see Fig. 6.1(a),(b) – cyan circle). Secondly, we observed protrusions in wide sites (see Fig. 6.1(a), (b) – red circle). These protrusions have triangular shape, therefore in the following text we will refer to them as  $Cu_1^{triang}$ . In STM movies we observed that these triangular protrusions hop around the wide site (see Fig. 6.2 – cyan rectangle). No DFT calculations were done, so we can only propose the structural model. The first possibility is that Cu atom sits above the Fe<sub>int</sub> atom closer to one oxygen atom and then hops over the Fe<sub>int</sub> atom to the other side. The second possibility is that Cu atom is incorporated in the first subsurface layer instead of a  $\mathrm{Fe}_{\mathrm{int}}$  atom, while  $\mathrm{Fe}_{\mathrm{int}}$  moved to subsurface cation vacancy. Then hopping observed in STM movie could be due to the hopping of Fe<sub>int</sub> atom between the cation vacancies underneath the wide site. When we deposited calibrated 0.2 ML of Cu, the calculated coverages from STM images were 0.21 ML and 0.07 ML for  $\text{Cu}_1^{\text{reg}}$  and  $\text{Cu}_1^{\text{triang}}$  adatoms, respectively. For deposition of calibrated 0.6 ML of Cu, it was 0.4 ML and 0.2 ML for for  $Cu_1^{reg}$  and  $Cu_1^{triang}$ , respectively. At low coverages the Cu atoms prefer regular narrow site for the adsorption, but for higher coverages, the amount of  $Cu_1^{\text{triang}}$  radically grows.



Figure 6.1: STM images of  $Cu/Fe_3O_4$ . In both the  $Cu_1^{reg}$  is highlighted by cyan circle and  $Cu_1^{triang}$  by red circle. (a) Our best resolved STM image of Cu. (b) Regular STM image of Cu.



Figure 6.2: Hopping of  $Cu_1^{triang}$  - cyan rectangle.

Copper is extraordinarily thermally stable. The incorporation of  $Cu_1$  adatoms starts at the temperature 450 °C. At this temperature, copper atoms prefer to be incorporated in  $Cu_{oct}(S)$  configuration (see Fig. 6.3(b)). The adatom coverage changed from initial 0.15 ML to 0.06 ML. The coverage of  $Cu_{oct}(S)$  structures (bright atoms in Fe<sub>oct</sub> rows) was 0.08 ML after heating to 450 °C and the coverage of  $Cu_{oct}(S-2)$  structures was 0.03 ML. After heating to 550 °C (Fig. 6.3(c)) the adatom coverage decreased to 0.02 ML.  $Cu_{oct}(S)$  structures almost completely disappeared and the surface became full of  $Cu_{oct}(S-2)$  structures. These results indicate that the  $Cu_{oct}(S-2)$  configuration is more favourable like it was for Rh.



Figure 6.3: (a)Initial state of  $Cu/Fe_3O_4(001)$  model catalyst. (b) The STM image of this system after heating to 450 °C. (c) The STM after additional heating to 550 °C.

We showed the outstanding thermal stability of copper adatoms on magnetite(001). But, there is another extraordinary thing about copper. Thanks to those two adsorption sites for copper atoms and the subsurface vacancies, we can deposit massive amount of copper on our sample and there still will be adatoms on the surface. Fig. 6.4(a) shows the STM image of 1 ML Cu deposited on Fe<sub>3</sub>O<sub>4</sub>(001) surface at room temperature. And we still can go higher with the coverage. In Fig. 6.4(b) is shown the STM image of 2.5 ML of Cu on magnetite(001).



Figure 6.4: (a)The STM image of 1.0 ML of Cu deposited on magnetite(001) at room temperature. (b) The STM image of 2.5 ML of Cu deposited on magnetite(001) at room temperature.

In [51] it was reported that  $Pt/Fe_3O_4(001)$  model catalyst shows promising results in CO and H<sub>2</sub> oxidation, but Pt adatoms sinter in CO atmosphere. Here, we tried to exploit highly saturated Cu adatom phase to trap the Pt<sub>1</sub>–CO carbonyls. We know that Pt<sub>1</sub> adatom becomes mobile after Pt<sub>1</sub>–CO carbonyl formation and forms clusters with other Pt<sub>1</sub> adatoms. This experiment is based on a simple thought, that when we fill all adsorption sites with Cu atoms, Pt<sub>1</sub>–CO carbonyls will be unable to move freely over the surface. Therefore we deposited 0.1 ML of Pt and on top of that 1.5 ML of Cu. We

## 6. $CU/FE_3O_4(001)$ MODEL CATALYST

started recording the STM movie in a CO background pressure  $p_{\rm CO}=8\times10^{-10}$  mbar. We were successful only partially in trapping Pt<sub>1</sub>–CO carbonyls. They are able to jump on Cu adatoms, but still the sintering rate was remarkably decreased. In Fig. 6.5(a) is shown the first image of the STM movie. Pt adatoms (Fig. 6.5(a) – cyan circles) are easily distinguished from Cu<sub>1</sub> adatoms, because they are much brighter. Fig. 6.5(b) shows the last image of the STM movie. This movie is so long that at this CO pressure the Pt<sub>1</sub> should be at normal conditions already sintered. But we still have many Pt<sub>1</sub>–CO carbonyls (red circles) on the surface. This was our first attempt to design the single atom catalyst, where we combined the behaviour of two different metals. Our studies so far show that there is no metal which is perfect in every aspect, but we can combine their properties to design the excellent single atom catalyst.



Figure 6.5: (a)The STM image (first image of a movie) of 0.1 ML of Pt and 1.5 ML of Cu deposited on magnetite(001) at room temperature. Pt<sub>1</sub> adatoms are brighter and few of them is highlighted by a cyan circle (b) The STM image (last image of a movie) acquired over the same sample area while we kept the background pressure of CO  $p_{\rm CO}=8\times10^{-10}$  mbar. Several Pt<sub>1</sub>-CO carbonyls are highlighted by a red circle.

Unfortunately, copper does not adsorb any of the gases we tried (CO, O<sub>2</sub>, NO and water). The heating experiments when we heated the  $Cu_1/Fe_3O_4(001)$  in these gases to 300 °C also showed no interaction.

# 7. Fe/TPA/Ag(111) model catalyst

This chapter is dedicated to the Fe/TPA/Ag(111) model catalyst prepared by molecular self-assembly. The first task was to synthesize a stable surface-confined structure consisting of single transition metal ions accessible for catalytic reactions. To achieve this we used terephthalic acid (TPA) (see Fig. 3.8) as a ligand in supramolecular network. Iron was used as coordinating atoms since it forms a stable iron dimer coordination motif carboxylate ligand (see Fig. 3.7 – red rectangle). Here, we present our experimental results.

## 7.1. Experimental details

These experiments were carried out in a brand new UHV complex system consisting of several chambers linked together via a single transfer line. In particular, we used 4 chambers, i.e., preparation chamber, deposition chamber, photoelectron spectroscopy chamber (PES) and scanning probe microscopy chamber (SPM) with base pressure under  $5 \times 10^{-10}$  mbar (for SPM chamber it was  $2 \times 10^{-10}$  mbar).

The preparation chamber was used solely to clean the single crystals (Ag(111), Ag(100) and Au(111)). The cleaning process consisted of cycles of sputtering with Ar<sup>+</sup> ions ( $p_{Ar} = 8 \times 10^{-6}$  mbar, high voltage = 3 kV, emission current = 10 mA, t = 20 min) followed by annealing with electron beam heating (for Ag crystals: T = 550 K, t = 10 min and for Au crystal: T = 650 K, t = 10 min). To clean the crystal we usually used 1 or 2 cycles, which was always enough to get a well defined clean surface.

Building blocks for metal-ligand coordination network were deposited on a freshly cleaned surface at 350 K using Near Ambient Temperature Effusion Cell NATC-40-10-HT-SHP (TPA) and Omicron single pocket electron beam evaporator (Fe) in the deposition chamber. Both evaporators were cooled with water to keep the pressure in the chamber under  $5 \times 10^9$  mbar. Unfortunately, a quartz crystal microbalance could not be used for the calibration of the deposition rate of TPA. The QCM measured that material was deposited on it, but we could not determine the amount due to the complexity of TPA molecule. For this should be used specialized thicknessmeter. Therefore, we could estimate the deposition rate only from STM measurements.

The analysis of the prepared samples was done in PES and SPM chambers. The analysis of freshly cleaned surface and the sample with deposited material was done by XPS and STM measurements. The PES chamber was equipped with XR50 X-ray source and PHOIBOS 100/150 hemispherical analyser from SPECS. The STM measurements were performed using SPM 150 Aarhus from SPECS at room temperature.

Firstly, it was necessary to test new equipment. The sputtering source and electron beam heater worked without any problems from the start. Complications occurred while using the NATC effusion cell. The water cooling system broke several times, which cost us a vast amount of experimental time. The XPS and STM worked quite well, but even though we achieved the atomic resolution in STM quite easily, there was still present noise in images due to insufficient damping. This is the why the STM images presented in this chapter do not have such a good image quality as was in the previous chapters.

The STM was tested on Au(111) single crystal because of its well known herringbone surface reconstruction [89]. The STM image of clean Au(111) surface is shown in Fig.

## 7.2. TEREPHTHALIC ACID SELF-ASSEMBLY ON AG(111)

7.1. Obviously, the noise lowers the image quality. Unfortunately, we were able to get rid of the noise only several times.



Figure 7.1: Atomic resolution STM image of the clean Au(111) surface.

## 7.2. Terephthalic acid self-assembly on Ag(111)

A common motif in organization of benzoic acids is hydrogen bonding of the self-complementary carboxyl groups [90]. In general, both flat-lying and upright-standing adsorption geometries are possible depending on the particular molecule used, substrate symmetry, molecular coverage and temperature. The observed configurations reflect deprotonation of the carboxyl groups, different carboxylate coupling schemes to the substrate and molecular interweaving hydrogen bonding.

The topology observed when TPA molecules were adsorbed on Ag(111) single crystal at 350 K is shown in Fig. 7.2(a). The molecules form regular domains ( $\sim 50$  nm) extended over entire terraces with almost perfect long-range ordering. The structure is built up from a square-shaped unit cell. The model of this structure is depicted in Fig. 7.2(b). Both carboxyl groups of TPA are deprotonated. The arrangement of molecules suggests hydrogen bonds between carboxylate oxygen and aromatic ring hydrogen. Every molecule is engaged in eight hydrogen bonds of the same type to its neighbours. Very similar adsorption geometry in this temperature range was also observed for Cu(100) substrate [91].

Afterwards, we proceeded with the calibration of the deposition rate. We tried many evaporation temperatures inside effusion and deposition times, but STM images always showed that the whole surface is covered with TPA. To determine the amount of deposited material by STM we needed the coverage under full monolayer. Unfortunately, due to

## 7. FE/TPA/AG(111) MODEL CATALYST

the time-consuming technique of determination of deposited amount and many technical problems we were unable to proceed with experimental study.



Figure 7.2: (a) The STM image of TPA deposited at 350 K on Ag(111). (b) Structural model of this adsorption geometry.

## 8. Conclusion

The aim of presented work was to experimentally study the interaction of gas molecules with single metal atoms by STM. The thesis starts with the brief introduction into the scanning tunneling microscopy. The reader is acquainted with the instrumentation and basic principles of this technique.

Afterwards, two approaches for preparation of stable surface-confined structures consisting of single transition metal atoms accessible for catalytic reactions are described. The first one is based on direct adsorption of metal atoms on a support strongly binding these atoms, thus preventing them from agglomeration into clusters. For this purpose,  $Fe_3O_4(001)$  single crystal was used. The  $\sqrt{2} \times \sqrt{2}$ )R45° surface reconstruction makes this support a perfect adsorption template for preparation of desired structures. The structural model explaining this phenomenon was presented. The second approach is based on self-assembly of metal atoms and organic molecules on metal surfaces. The reader is introduced to the field of molecular self-assembly from the basics to more complex topics focused mainly on metal-ligand coordination networks.

The experimental part begins with the description of Rh/Fe<sub>3</sub>O<sub>4</sub>(001) model catalyst. It is mainly focused on real-time behaviour and thermal stability of Rh species. The STM measurements revealed the presence of three rhodium species on the surface. First ones are regular Rh<sub>1</sub><sup>reg</sup> adatoms, which are under UHV conditions stable. These adatoms can dissociate water molecules present in the chamber and form Rh<sub>1</sub>–O<sub>w</sub>H hydroxyls. They have different apparent morphology from Rh<sub>1</sub><sup>reg</sup> adatoms, thus we are able to easily distinguish between these two rhodium species in STM images. We showed the desorption of O<sub>w</sub>H hydroxyl group from Rh adatom induced by scanning at high bias voltages. Lastly, when two Rh atoms adsorb at the same place during deposition, the Rh<sub>2</sub><sup>osc</sup> dimer is formed. These dimers undergo oscillation around the adsorption site in Fe<sub>oct</sub> row direction. We found out that upon annealing to 250 °C, the rhodium atoms are incorporated into the surface in two configurations, i.e., Rh<sub>oct</sub>(S) and Rh<sub>oct</sub>(S-2).

It is well known that magnetite(001) surface can split water molecules at room temperature. Our experiments showed that Rh species present on the surface markedly assist in water dissociation.  $Rh_2^{osc}$  dimers can adsorb CO molecules. These two facts are key prerequisites for application of  $Rh/Fe_3O_4(001)$  model catalyst as a potential water gas shift catalyst. Nevertheless, there are open issues which should be addressed before it will possible to use it in real systems. Major issue is insufficient amount of active sites for CO adsorption. Our experiments showed that Rh adatoms agglomerate into clusters upon exposure to  $O_2$  atmosphere. Unfortunately,  $Rh_2$  dimers formed by sintering are not active in CO molecule adsorption. Lastly, this system showed very high activity in NO molecule adsorption.

The second studied model catalyst  $(Ir/Fe_3O_4(001))$  showed very similar behaviour. Iridium atoms also exist in adatom phase as well as dimers upon deposition on magnetite(001) surface. This system is active in NO adsorption and sinters in O<sub>2</sub> atmosphere. But on the other hand, it does not interact with CO and no change in rate of water splitting was observed with Ir species present on the surface. In general, its interaction with studied gases is considerably weaker.

The last studied model catalyst prepared by direct deposition of metal atoms on strongly binding substrate was  $Cu/Fe_3O_4(001)$ . Copper atoms adsorb on magnetite(001) surface in two configurations and moreover are very stable. This fact allowed us to prepare

highly saturated Cu adatom phase. We tried to utilize high stability a inreactivity of Cu adatoms in our first attempt to design the model catalyst with desired properties. We were only partially successful.

Unfortunately, we were unable to prepare and study the system based on metal-ligand coordination networks. At least, we showed the deprotonation of TPA upon deposition on Ag(111) single crystal at 350 K. But we were able to test the new equipment and start with the experimental work, which will be continued in the future. This project has a good potential to achieve great results in the field of molecular self-assembly and single atom catalysis.

To conclude, STM proved to be effective technique in unravelling several mechanisms of interaction of gas molecules with single metal atoms. Moreover, we presented several results that have the possibility for application in single atom catalysis.

# 9. Bibliography

- WEISZ, P. B., HAAG, W. O., RODEWALD, P. G.: Catalytic production of highgrade fuel (gasoline) from biomass compounds by shape-selective catalysis. *Science*, 1979, vol. 206, p. 57-58.
- [2] FURUTA, S., MATSUHASHI, H., ARATA, K.: Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catalysis Communications*, 2004, vol. 5, p. 721-723.
- [3] BONET-RAGEL, H., et al.: Synthesis of biodiesel from high FFA alperujo oil catalysed by immobilised lipase. *Fuel*, 2015, vol. 161, p. 12-17.
- [4] BLASER, H. U.: Heterogeneous catalysis for fine chemicals production. Catalysis Today, 2000, vol. 60, p. 161-165.
- [5] BLASER, H. U.: Enantioselective catalysis in fine chemicals production. *Chemical Communications*, 2003, vol. 3, p. 293-296.
- [6] TUCKER, C. E., de VRIES, J. G.: Homogeneous catalysis for the production of fine chemicals. Palladium- and nickel-catalysed aromatic carbon-carbon bond formation. *Topics in Catalysis*, 2002, vol. 19, p. 111-118.
- [7] YANG, H. F., et al.: Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis. Accounts of Chemical Research, 2013, vol. 46, p. 1740-1748.
- [8] FLYTZANI-STEPHANOPOULOS, M., GATES, B. C.: Atomically Dispersed Supported Metal Catalysts. Annual Review of Chemical and Biomolecular Engineering, 2012, vol. 3, p. 545-574.
- [9] HARUTA, M., et al.: Low-temperature oxidation of CO over gold supported on TiO<sub>2</sub>. Journal of Catalysis, 1993, vol. 144, p. 175-192.
- [10] QIAO, B. T., et al.: Single-atom catalysis of CO oxidation using Pt<sub>1</sub>/FeO<sub>x</sub>. Nature Chemistry, 2011, vol. 3, p. 634-641.
- [11] LI, Z. Y., et al.: CO Oxidation Catalyzed by Single Gold Atoms Supported on Aluminum Oxide Clusters. *Journal of the American Chemical Society*, **2014**, vol. 136, p. 14307-14313.
- [12] LIN, J., et al.: Remarkable Performance of Ir<sub>1</sub>/FeO<sub>x</sub> Single-Atom Catalyst in Water Gas Shift Reaction. Journal of the American Chemical Society, 2013, vol. 135, p. 15314-15317.
- [13] FLYTZANI-STEPHANOPOULOS, M.: Gold Atoms Stabilized on Various Supports Catalyze the Water-Gas Shift Reaction. Accounts of Chemical Research, 2014, vol. 47, p. 783-792.
- [14] FEYNMAN, R. P.: There's Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics. Lecture at an 1959 APS meeting. The Archives, California, Institute of Technology, see www.its.caltech.edu/ feynman/plenty.html 1959.

- [15] BINNIG, G., ROHRER, H., GERBER, C., and WEIBEL, E.: Tunneling through a controllable vacuum gap. *Applied Physics Letters*, **1982**, vol. 40, p. 178-180.
- [16] BINNIG, G., ROHRER, H., GERBER, C., and WEIBEL, E.: Surface studies by scanning tunneling mocroscopy. *Physical Review Letters*, **1982**, vol. 49, p. 57-61.
- [17] BINNIG, G., ROHRER, H., GERBER, C., and WEIBEL, E.: 7×7 reconstruction on Si(111) resolved in real space. *Physical Review Letters*, **1983**, vol. 50, p. 120-123.
- [18] BINNIG, G., QUATE, C. F., GERBER, C.: Atomic force microscope. *Physical Review Letters*, **1986**, vol. 56, p. 930-933.
- [19] BINNIG, G., ROHRER, H.: Scanning tunneling microscopy from birth to adolescence. Reviews of Modern Physics, 1987, vol. 59, p. 615-625.
- [20] BINNIG, G., ROHRER, H.: In touch with atoms. Reviews of Modern Physics, 1999, vol. 71, p. S324-S330.
- [21] STIPE, B. C., REZAEI, M. A., HO, W.: Inducing and viewing the rotational motion of a single molecule. *Science*, **1998**, vol. 279, p. 1907-1909.
- [22] HEINRICH, A. J., et al.: Single-atom spin-flip spectroscopy. Science, 2004, vol. 306, p. 466-469.
- [23] HIRJIBEHEDIN, C. F., LUTZ, C. P., HEINRICH, A. J.: Spin coupling in engineered atomic structures. *Science*, 2006, vol. 312, p. 1021-1024.
- [24] BALASHOV, T., et al.: Magnetic Anisotropy and Magnetization Dynamics of Individual Atoms and Clusters of Fe and Co on Pt(111). *Physical Review Letters*, 2009, vol. 102.
- [25] KHAJETOORIANS, A. A., et al.: Itinerant Nature of Atom-Magnetization Excitation by Tunneling Electrons. *Physical Review Letters*, **2011**, vol. 106.
- [26] WU, S. W., OGAWA, N., HO, W.: Atomic-scale coupling of photons to singlemolecule junctions. *Science*, 2006, vol. 312, p. 1362-1365.
- [27] ZHOU, L., et al.: Strength and directionality of surface Ruderman-Kittel-Kasuya-Yosida interaction interaction mapped on the atomic scale. *Nature Physics*, 2010, vol. 6, p. 187-191.
- [28] KHAJETOORIANS, A. A., et al.: Atom-by-atom engineering and magnetometry of tailored nanomagnets. *Nature Physics*, **2012**, vol. 8, p. 497-503.
- [29] WIKIPEDIA, [online], see https://en.wikipedia.org/wiki/Scanning\_tunneling\_microscope, **2016**.
- [30] QUATE, C. F.: Vacuum Tunneling: A New Technique for Microscopy. *Physics Today*, 1986, vol. 39, p. 26-33.
- [31] TERSOFF, J., HAMANN, D. R.: Theory of the scanning tunneling microscope. *Physical Review B*, **1985**, vol. 31, p. 805-813.

- [32] PENDRY, J. B., PRETRE, A. B., KRUTZEN, B. C. H.: Theory of the scanning tunneling microscope. *Journal of Physics - Condensed Matter*, **1991**, vol. 3, p. 4313-4321.
- [33] BARDEEN, J.: Tunneling from a many-particle point of view. *Physical Review Letters*, 1961, vol. 6, p. 57.
- [34] WEISS, W., RANKE, W.: Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers. *Progress in Surface Science*, 2002, vol. 70, p. 1-151.
- [35] LI, S. Z., et al.: Promoted iron-based catalysts for the Fischer-Tropsch synthesis: Design, synthesis, site densities, and catalytic properties. *Journal of Catalysis*, 2002, vol. 206, p. 202-217.
- [36] COELHO, F. D., et al.: Potential application of highly reactive Fe(0)/Fe<sub>3</sub>O<sub>4</sub> composites for the reduction of Cr(VI) environmental contaminants. *Chemosphere*, 2008, vol. 71, p. 90-96.
- [37] ZHANG, Z., SATPATHY, S.: Electron-States, Magnetism, and the Verwey Transition in Magnetite. *Physical Review B*, **1991**, vol. 44, p. 13319-13331.
- [38] YOON, K. S., et al.: Performance of Fe<sub>3</sub>O<sub>4</sub>/AlO<sub>x</sub>/CoFe magnetic tunnel junctions based on half-metallic Fe<sub>3</sub>O<sub>4</sub> electrodes. *Journal of Magnetism and Magnetic Materials*, **2005**, vol. 285, p. 125-129.
- [39] PARK, C., et al.: Inverse magnetoresistance in magnetic tunnel junction with an Fe<sub>3</sub>O<sub>4</sub> electrode. *IEEE Transactions on Magnetics*, **2005**, vol. 41, p. 2691-2693.
- [40] MANTOVAN, R., et al.: CVD synthesis of polycrystalline magnetite thin films: structural, magnetic and magnetotransport properties. *Journal of Physics D-Applied Physics*, 2010, vol. 43, p. 11-21.
- [41] SCHMIDT, G., et al.: Fundamental obstacle for electrical spin injection from a ferromagnetic metal into diffusive semiconductor. *Physical Review B*, 2000, vol. 62, p. R4790-R4793.
- [42] DEDIU, V., et al.: Room temperature spin polarized injection in organic semiconductor. Solid State Communications, 2002, vol. 122, p. 181-184.
- [43] PARKINSON, G. S., et al.: A metastable Fe(A) termination at the Fe<sub>3</sub>O<sub>4</sub>(001) surface. Surface Science, 2011, vol. 605, p. L42-L45.
- [44] KIM, Y. J., GAO, Y., CHAMBERS, S. A.: Selective growth and characterization of pure, epitaxial α-Fe<sub>2</sub>O<sub>3</sub>(0001) and Fe<sub>3</sub>O<sub>4</sub>(001) films by plasma-assisted molecular beam epitaxy. *Surface Science*, **1997**, vol. 371, p. 358-370.
- [45] VOOGT, Y. J., et al.: NO<sub>2</sub>-assisted molecular-beam epitaxy of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3- $\delta$ </sub>O<sub>4</sub>, and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> thin films on MgO(100). *Physical Review B*, **1999**, vol. 60, p. 11193-11206.
- [46] STANKA, B., et al.: Surface reconstruction of  $Fe_3O_4(001)$ . Surface Science, 2000, vol. 448, p. 49-63.

- [47] PARKINSON, G. S., et al.: Semiconductor-half metal transition at the Fe<sub>3</sub>O<sub>4</sub>(001) surface upon hydrogen adsorption. *Physical Review B*, **2010**, vol. 82, p. 5.
- [48] BLIEM, R., et al.: Subsurface cation vacancy stabilization of the magnetite (001) surface. Science, 2014, vol. 346, p. 1215-1218.
- [49] NOVOTNY, Z., et al.: Ordered Array of Single Adatoms with Remarkable Thermal Stability: Au/Fe<sub>3</sub>O<sub>4</sub>(001). *Physical Review Letters*, **2012**, vol. 108.
- [50] BLIEM, R., et al.: Cluster Nucleation and Growth from a Highly Supersaturated Adatom Phase: Silver on Magnetite. ACS Nano, 2014, vol. 8, p. 7531-7537.
- [51] BLIEM, R., et al.: An Atomic-Scale View of CO and H<sub>2</sub> Oxidation on a Pt/Fe<sub>3</sub>O<sub>4</sub> Model Catalyst. Angewandte Chemie-Int. Ed., 2015, vol. 54, p. 13999-14002.
- [52] PARKINSON, G. S., et al.: Carbon monoxide-induced adatom sintering in a Pd-Fe<sub>3</sub>O<sub>4</sub> model catalyst. *Nature Materials*, **2013**, vol. 12, p. 724-728.
- [53] WHITESIDES, G. M., GRZYBOWSKI, B.: Self-assembly at all scales. Science, 2002, vol. 295, p. 2418-2421.
- [54] FELHOSI, I., KALMAN, E., POCZIK, P.: Corrosion protection by self-assembly. Russian Journal of Electrochemistry, 2002, vol. 38, p. 230-237.
- [55] BAIN, C. D., WHITESIDES, G. M.: Modeling organic-surfaces with self-assembled monolayers. Angewandte Chemie Int. Ed., 1989, vol. 28, p. 506-512.
- [56] LAIBINIS, P. E., WHITESIDES, G. M.: Self-assembled monolayers of nalkanethiolates on copper are barrier films that protect the metal against oxidation by air. *Journal of American Chemical Society*, **1992**, vol. 114, p. 9022-9028.
- [57] BOHRINGER, M., et al.: Two-dimensional self-assembly of supramolecular clusters and chains. *Physical Review Letters*, **1999**, vol. 83, p. 324-327.
- [58] LUKAS, S., WITTE, G., WOLL, C.: Novel mechanism for molecular self-assembly on metal substrates: unidirectional rows of pentacene on Cu(110) produced by a substrate-mediated repulsion. *Physical Review Letters*, **2002**, vol. 88.
- [59] WECKESSER, J., et al.: Mesoscopic correlation of supramolecular chirality in onedimensional hydrogen-bonded assemblies. *Physical Review Letters*, 2001, vol. 87.
- [60] THEOBALD, J. A., et al.: Controlling molecular deposition and layer structure with supramolecular surface assemblies. *Nature*, **2003**, vol. 424, p. 1029-1031.
- [61] PAWIN, G., et al.: A homomolecular porous network at a Cu(111) surface. Science, 2006, vol. 313, p. 961-962.
- [62] STEPANOW, S., et al.: Steering molecular organization and host-guest interactions using two-dimensional nanoporous coordination systems. *Nature Materials*, 2004, vol. 3, p. 229-233.
- [63] BARTH, J. V., CONSTANTINI, G., KERN, K.: Engineering atomic and molecular nanostructures at surfaces. *Nature*, 2005, vol. 437, p. 114-116.

- [64] KUHNLE, A.: Self-assembly of organic molecules at metal surfaces. Current Opinion in Colloid and Interface Science, 2007, vol. 14, p. 157-168.
- [65] MAKSYMOVYCH, P., et al.: Gold-adatom-mediated bonding in self-assembled short-chain alkanethiolate species on the Au(111) surface. *Physical Review Letters*, 2006, vol. 97, p. 146103-146104.
- [66] SIEGEL, J. S.: Supramolecular Chemistry: Concepts and Perspectives. Science, 2007, vol. 271, p. 949-949.
- [67] LAWRENCE, D. S., JIANG, T., LEVETT, M.: Self-Assembling Molecular Complexes. *Chemical Reviews*, **1995**, vol. 95, p. 2229-2260.
- [68] SWIEGERS, G. F., MALEFETSE, T. J.: New self-assembled structural motifs in coordination chemistry. *Chemical Reviews*, 2000, vol. 100, p. 3483-3537.
- [69] LEININGER, S., OLENYUK, B., STANG, P. J.: Self-assembly of discrete cyclic nanostructures mediated by transition metals. *Chemical Reviews*, **2000**, vol. 100, p. 853-907.
- [70] STEPANOW, S., LIN, N., BARTH, J. V.: Modular assembly of low-dimensional coordination architectures on metal surfaces. *Journal of Physics: Condensed Matter*, 2008, vol. 20.
- [71] BERSUKER, I. B.: Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory. New York: Wiley, 1996, ISBN 04-711-3079-6.
- [72] BARTELS, L.: Tailoring molecular layers at metal surfaces. Nature Chemistry, 2010, vol. 2, p. 87-95.
- [73] YANASE, A., HAMADA, N.: Electronic structure in high temperature phase of Fe<sub>3</sub>O<sub>4</sub>. Journal of Physical Society of Japan, **1999**, vol. 68, p. 1607-1613.
- [74] PARKINSON, G. S., et al.: Room Temperature Water Splitting at the Surface of Magnetite. Journal of the American Chemical Society, 2011, vol. 133, p. 12650-12655.
- [75] BLIEM, R., et al.: Adsorption and incorporation of transition metals at the magnetite Fe<sub>3</sub>O<sub>4</sub>(001) surface. *Physical Review B*, **2015**, vol. 92.
- [76] DUJARDIN, G., WALKUP, E., AVOURIS, P.: Dissociation of individual molecules with electrons from the tip of a scanning tunneling microscope. *Science*, **1992**, vol. 255, p. 1232-1235.
- [77] STOKBRO, K., et al.: STM-induced hydrogen desorption via a hole resonance. *Physical Review Letters*, **1998**, vol. 80, p. 2618-2621.
- [78] LI, F., LI, Y., ZENG, X. C., CHEN, Z.: Exploration of High-Performance Single-Atom Catalysts on Support M<sub>1</sub>/FeO<sub>x</sub> for CO oxidation via Computational Study.ACS Catalysis, 2015, vol. 5, p. 544-552.

- [79] PHILIPSEN, P. H. T., et al.: Relativistic calculations on the adsorption of CO on the (111) surfaces Ni, Pd and Pt within the zeroth-order regular approximation. *Physical Review B*, **1997**, vol. 56, p. 13556-13562.
- [80] CURULLA, D., et al.: A density functional theory of the adsorption of CO on Rh(111). Physical Chemistry Chemical Physics, 2002, vol. 21, p. 5372-5376.
- [81] KITTEL, C.: Introduction to Solid State Physics. 8th Edition, Hoboken, 2005, ISBN 978-0471415268, p. 50.
- [82] RATNASAMY, C., WAGNER, J. P.: Water Gas Shift Catalysis. *Catalysis Reviews*, 2009, vol. 51, p. 325-440.
- [83] THIEL, P. A., SHEN, M., LIU, D. J., EVANS, J. W.: Adsorbate-enhanced transport of metal surfaces: Oxygen and sulfur on coinage metals. *Journal of Vacuum Science* & *Technology A*, 2010, vol. 28, p. 1285-1298.
- [84] LIANG, J. X., et al.: Theoretical and Experimental Investigations on Single-Atom Catalysis: Ir<sub>1</sub>/FeO<sub>x</sub>. The Journal of Physical Chemistry C, 2014, vol. 118, p. 21945-21951.
- [85] QIAO, B., et al.: Single-atom catalysis of CO oxidation using Pt<sub>1</sub>/FeO<sub>x</sub>.Nature Chemistry, 2011, vol. 3, p. 634-641.
- [86] GHOSH, T. K., NAIR, N. N.: Rh<sub>1</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Single-Atom Catalysis of O<sub>2</sub> Activation and CO Oxidation: Mechanism, Effects of Hydration, Oxidation State, and Cluster Size. ChemCatChem, **2013**, vol. 5, p. 1811-1821.
- [87] SHELEF, M., McCABE, R. W.: Twenty-five years after introduction of automotive catalysis: what next? *Catalysis Today*, 2000, vol. 62, p. 35-50.
- [88] TANG, Y., et al.: Adsorption behaviour of Co anchored on graphene sheets toward NO, SO<sub>2</sub>, NH<sub>3</sub> and HCN molecules. *Applied Surface Science*, **2015**, vol. 342, p. 191-199.
- [89] BARTH, J. V., BRUNE, H., ERTL, G., BEHM, R. J.: Scanning tunneling microscopy observations on the reconstructed Au(111) surface – atomic structure, long-range superstructure, rotational domains, and surface defects. *Physical Review B*, 1990, vol. 42, p. 9307-9318.
- [90] DMITRIEV, A., et al.: Supramolecular assemblies of trimesic acid on a Cu(100) surface. Journal of Physical Chemistry B, 2002, vol. 106, p. 6907-6912.
- [91] STEPANOW, S., et al.: Deprotonation-Driven Phase Transformations in Terephthalic Acid Self-Assembly on Cu(100). Journal of Physical Chemistry B, 2004, vol. 108, p. 19392-19397.