Investigation of oxide-metal interaction and alloying processes on Rh(111) and TiO$_2$(110) with scanning tunnelling microscopy

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PhD Thesis

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INTRODUCTION

Surface chemistry can be described as an interdisciplinary field of research in physics, chemistry, and engineering. Since the 1960s onwards, there has been a rapid development of surface sciences, largely attributed to the emergence of more sophisticated microelectronics and computing tools and engineering equipment. In addition, the development and technical implementation of ultravacuum technology, the developed electron spectroscopic and surface microscopy methods have opened a new path for the molecular examination of surfaces and interfaces. At the same time surface science started to implement and to exploit the achievements of modern quantum theory, creating new and more accurate results, allowing for a more sophisticated examination of chemical processes and reactions occurring on solid surfaces. Today, surface chemistry, combined with theoretical and experimental research, can create new concepts, and produce innovative results that are no longer limited to solid materials. Surface chemistry is a well-developed field of natural sciences, which currently focuses on the study of electrons and molecules, various excitation states, on a few tenths of a nanometer size and femtosecond time scale, and tries to understand and control surface structures and surface chemical reactions at a molecular level. It is important to mention that, for several years, a substantial portion of the world's GDP has involved surface chemistry, surface chemical innovations and related developments. The most important of these are the semiconductor industry, petrochemical industry, heterogeneous catalysis, and automotive industries. In today's modern and emerging technologies, surface chemistry also plays a key role, in the design and production of photovoltaic devices, semiconductors and coating technologies, biomedical devices, fuel cells, investigation and development of self-supporting, self-limiting ultrathin layers[1,2].

In heterogeneous catalysis a catalyst is a substance that accelerates the chemical reaction while remaining unchanged. In a reaction with a number of possible products, the catalyst may facilitate the formation of a particular product, which is described as the selectivity of the catalyst. Heterogeneous catalytic reactions occur in the outermost surface (atomic) layers of the solid catalyst during elemental, surface chemical steps such as adsorption, surface diffusion, the surface reaction

itself and the desorption of the products from the surface[1]. It was surface sciences which made the most significant contribution to the understanding of these chemical reactions at the fundamental level[3–8]. As a result, it was even possible to identify the intermediates, the elemental surface reaction steps and the regarding reaction kinetics parameters (e.g. reaction rate constant, activation energies) and the catalytically active centers of the of the catalyst[2]. In heterogeneous catalysis, the catalyst itself is typically a combination of a support and a catalytically active metal. Under laboratory conditions, metal and oxide single crystals can be used to model the industrial heterogeneous catalytic processes under controlled reaction conditions.

The first materials used in surface science research were metal surfaces, followed by oxides and ultrathin oxide on metals (UTO - ultrathin oxide) which have been the subject of surface chemistry research over the last 30 years[9,10]. The spectacular attention to the self-supporting graphene[11] and hexagonal[12] boron nitride stimulated also the research of atomically thin non-oxidic 2D layers[13,14] starting from the first decade of this millennium. Returning back to the previous discussion, two-dimensional oxides, ultra-thin layers, metallic and bimetallic nano and surface alloys dispersed at the atomic level provide an excellent basis for both fundamental and practical research[15] in homogeneous[16], heterogeneous[3,17–21], photo[22,23] and electrochemical[20,24,25] catalysis for fine-tuning the catalyst's active centres and investigating their advantageous properties. By systematically studying appropriate model systems, it is possible to establish the connection between their structure and activity[3–8].

The exceptional and enhanced catalytic properties of alloyed, bimetallic systems arise from the synergistic properties of the two metals. Indeed, the relationship between the surface free energies and work functions of the metals and their support plays a crucial role in surface and subsurface processes[26]. The structure and versatile composition of these nanoparticles are largely determined by the nanoscale thermodynamics and kinetic processes[27,28]. The formation of bimetallic NPs on (reducible) oxides is a rather complex process. On reducible oxide supports one also has to consider the encapsulation of the supported metal nanoparticles by the reduced phase of the oxide[29,30]. All these physicochemical variables which make these material systems

rather complex also give the opportunity for us to fine tune their properties[31–38].

The prominent study of ultrathin oxide layers can be traced back to a very interesting phenomenon in heterogeneous catalysis around the 1970s, which has been described in the literature as the strong metal-support interaction (SMSI), decoration or encapsulation process[38]. In general, the encapsulation of the supported metal nano-particles degrades their catalytic activity (H and CO adsorption) by decreasing the number of the catalytically active sites in case of supported VIII.B metals (Ir, Rh, Ni, Pd and Pt) on easily reducible oxide supports (TiO_2, TaO_5, CeO_2,NbO). In this process the catalytically active sites of the metal nanoparticles are covered by the atomically thin reduced phase of the oxide support.

It is indisputable that the material systems described above have major influence on the economy, industry, research and development and on our daily lives. Therefore, examination and deeper understanding of key factors influencing the build-up of these systems are crucial in the science of the twenty-first century.

One of the aims of my dissertation is to describe and discuss the material transport processes of strong metal-support interaction, surpassing the current results of international research. In the experiments I used $TiO_2(110)$ single crystals as oxide support and transition metals suitable for decoration (Rh, Pd). In this context, I would like to provide a detailed description of the structure of the TiO_x ultrathin two-dimensional oxide film on Rh. Similar studies have been conducted on Pd nanoparticles supported on $TiO_2(110)$. One of the strengths of my dissertation is the possibility of comparing the behavior of these fundamentally similar yet different in detail oxide-metal systems. Furthermore, I have studied the preferential adsorption sites of Au atoms on the (2D) TiO_x films to demonstrate their application as nanotemplates. In addition, the comprehensive study of Rh-Au bimetallic nanoalloys and the interaction of the above oxide-metal systems with Au are also an integral part of this dissertation. The most important experimental method used in this work was scanning tunnel microscopy, but in the evaluation of my results I also rely on the experimental and theoretical work carried out in cooperation with my colleagues over the course of the study of the same systems.

APPLIED EXPERIMENTAL TECHNIQUES

The results presented in this work were obtained using two different ultrahigh vacuum (UHV) chambers. The first one can be found in the SPM (Scanning Probe Microscopy) laboratory at the University of Szeged, equipped with a room temperature scanning tunnelling microscope (STM), while the second one at the Nanoscience group of University College London, which contained a variable temperature STM, and a combined, low energy electron diffraction (LEED) – Auger electron spectrometer. The $TiO_2(110)$ rutile (Pi-Kem) and Rh(111) (MaTeck) single crystals were cleaned using cycles of argon ion sputtering (1.5 keV) and annealing in vacuum at 1000 K and 1250 K, respectively. In the case of rhodium in order to avoid carbon contamination, annealing in low pressure oxygen atmosphere was also applied. For the different metal loads (Rh, Au, Pd) a designated physical vapor deposition was used. The coverage of Rh, Pd and Au is expressed in monolayers (ML), defined as the surface concentration of Rh(111), Pd(111) and Au(111), respectively (for Rh 1 ML~1.60×10^{15} atoms/cm^2, for Pd 1 ML~1.54×10^{15} atoms/cm^2 and for Au 1 ML ~ 1.39×10^{15} atoms/cm^2). STM images were recorded in constant current and constant height mode using W tips prepared by electrochemical etching and conditioning by voltage pulses in STM. The STM images were analysed using SPIP and WSxM software[39]. For determining the average height, at least one hundred nanoparticles were measured.

RESULTS - THESES

1.1 I proved that by increasing the amount of gold on Rh(111) at 500 K, the Au basically shows 2D "layer-by-layer" growth and character. At smaller gold coverages the preferential adsorption (nucleation) sites are the step edges of Rh(111), where the growth of the layer starts toward the lower laying Rh terraces ("step-flow"). After the formation of the first layer a one-dimensional (1D) rhodium-gold interface is created, which can function as nucleation site in the further gold deposition. This way the second gold layer grows on the first layer initially located on the upper Rh terraces. Deposition of 1 ML Au is not enough to totally cover the full surface area of Rh(111), whereas dosing 1.2 ML Au the layer exhibit holes with app. 20% of the total covered area. *(PhD01)*

1.2 I observed that after 0.8 ML gold deposition (500 K) and annealing (800 K) the measured nearest neighbour atom distance in the first gold layer is equal to the Rh(111) nearest neighbour atom distance, which indicates a pseudomorph growth and arrangement. This effect strongly connects with the mixing of the topmost atomic layers of Au and Rh (surface alloy formation). At 4 ML Au coverages the measured nearest neighbour distance corresponds to the expected Au(111) bulk value. *(PhD01)*

1.3 Despite the fact that the Rh does not form bulk alloy with Au, I detected the formation of ordered surface alloy. After 0.8 ML Au deposition (500 K) and annealing (1000 K) laterally limited domains from with (2×1) arrangement. I proposed a structural model for the (2×1) surface alloy, (conformed with theoretical calculations) where the Au and Rh atomic rows alternates in the same plane, in other words, the Au incorporates into the Rh(111) terraces. *(Phd01, PhD04)*

2.1 I gave a more precise structural model for the previously described, ordered $TiO_{\sim 1.2}$ oxide layer on $TiO_2(110)\backslash Rh$. This oxide layer can be easily formed on rutile supported 50-100 nm Rh (111) planes by annealing at 1000 K in UHV. As a result of the decoration process a specially ordered, atomically thin $TiO_{\sim 1.2}$ pinwheel oxide layer with

hexagonal periodicity, which has a 1.66 nm supercell cell constant. On the STM images the oxide layer exhibits dots with brighter and darker contrast, where each dot corresponds to a Ti ion with an average 0.31 nm nearest neighbour distance in close packed, hexagonal arrangement. A characteristic feature of the pinwheel structure is the 15 and 21 atom created equilateral triangle, where the sides of the triangle consists of 5 and/or 6 Ti ions with brighter contrast on the constant height STM images. These Ti ions are coordinated with four oxygen ions from top, while the rest with three. This inhomogeneous oxygen distribution is responsible for the experienced chemical contrast and the broken stoichiometry of the layer. (To draw these conclusions, I also relied on our X-ray photoelectron spectroscopy, XPS and low energy ion scattering spectroscopy, LEIS and DFT results.) *(PhD03)*

2.2 With room temperature sub monolayer (~0.05 MR) Au adsorption I proved that the cover of supported Rh(111) facets, namely the $TiO_{\sim1.2}$ layer can be used as nanotemplate for gold nanoparticles. At the contacting areas of the equilateral triangles the layer exhibits preferential adsorption sites in the means of the impinging Au atoms, thus it is possible to create Au nanoparticles consisting of 6-8 Au atoms, with 1.66 nm average distance, periodically in hexagonal arrangement. *(PhD03, PhD05)*

2.3 With the analysis of the STM z-line profiles I showed that after 0.3 ML Au load onto the $TiO_{\sim1.2}$ layer at 300 K, the Au nucleates on the top of the decoration layer. These nanoparticles have an 0.24 nm average height, which is the height of one atomic layer of Au(111). In contrast, dosing the same amount at 500 K, results in the decrease in the average height of the nanoparticles (0.15 nm). At higher temperature the Au penetrates though the oxide layer and bonds directly to the Rh(111) underneath. Thus, indirectly the apparent thickness of the oxide layer can be determined, which is ~0.1 nm. *(PhD05)*

2.4 I found that at higher Au loads (1 ML and 1.5 ML) at 500 K the nanoparticles exhibit 3D morphology. With stepwise annealing these nanoparticles spread out and form a 2D layer with hexagonal and round shaped morphology. Depending on the coverage with 0.5 ML it is

possible to form a pseudomorph (1×1) and >0.8 ML (2×1) alloyed structures. Some of these NPs can be partially covered with a second Au layer. Using this method, a 1D oxide-metal (TiO$_{\sim1.2}$-Au) interface can be created which can serve as an excellent model system for further catalytic and gas adsorption studies. *(PhD05)*

2.5 With 30 ML Rh deposition (500 K) onto TiO$_2$(110) a continuous film was created, which also showed the TiO$_{\sim1.2}$ decoration layer after 900 K annealing. I found that with deposition of 3 ML Au (500 K) onto the continuous rhodium film the encapsulation by the oxide layer can be prevented. The gold somehow seals the surface and blocks the segregation, diffusion of Ti and O atoms at higher temperatures to the surface. Around 900 K-1000 K nanodots appear on the surface with characteristic 2-3 nm diameter. By using the findings of our research group (XPS and LEIS) these surface structures were identified as TiO$_2$ nanodots. At this temperature the oxidation of the previously segregated Ti atoms happens by the oxygen coming from the bulk of rutile. In the tested temperature range, the formation of ordered oxide layer on the topmost atomic layer was not detected. *(PhD06)*

3.1 With 5 ML Pd and 1 ML Au deposition at 300 K on TiO$_2$(110) Au-Pd bimetallic nanoparticles were formed. Applying STM, AES and LEED I showed that these NPs have a Au-Pd core Pd shell structure and are further encapsulated by a TiO$_x$ decoration layer after annealing at 900 K. On the top surface layer, the pinwheel and zig-zag structures were detected. The pinwheel structure shows an average 0.33 nm nearest neighbour distance in the means of Ti ions, with 1.70 nm superlattice periodicity, while the interatomic distance in the zig-zag type are 0.29 nm and 0.31 nm, with 0.80 nm×0.66 nm lattice parameters. These two types of the decoration layers form domains, which are being continuously transformed into one another. *(PhD02)*

3.2 I found that with increasing the Au/Pd ratio (dosing 2 ML Au to 3 ML Pd at 300 K) on TiO$_2$(110) and annealing (973 K) Au-Pd core and Au shell NPs form. According to the STM and LEED results

these bimetallic nanoparticles have regular hexagonal morphology where top facet appears to be essentially close packed Au(111). *(PhD02)*

3.3 I have concluded from STM measurements that depositing 0.1 ML gold onto the encapsulation layer (see 3.1 thesis point) at 300 K the gold nucleates preferentially at the pico-hole regions, in the middle of the pinwheels. The measured average height of the NPs is 0.15 nm which indicates that the gold penetrates through the layer and binds to the Pd(111) underneath at room temperature. Over 873 K the gold NPs completely disappear from the surface, which is due to the diffusion of Au into the Pd bulk. This explanation can be rationalized if one considers the fact that Pd shows high bulk miscibility with Au, moreover at this temperature the Au cannot desorb from the surface. *(PhD02)*

3.4 According to my results, it can be concluded that the encapsulation by the reduced phase of titania can be prevented by adequate amount deposition of Au on Rh and Pd nanoparticles formed on TiO_2(110) support. *(PhD02, PhD06)*

LIST OF PUBLICATIONS RELEVANT TO THIS THESYS

PhD01.   K. Palotás, L. Óvári, G. Vári, **R. Gubó**, A. P. Farkas, J. Kiss, A. Berkó, Z. Kónya; *Au- Rh surface structures on Rh(111): DFT insights to the formation of an ordered surface alloy;* JOURNAL OF PHYSICAL CHEMISTRY C (2018)
IF: 4.536; MTMT [3422662]

PhD02.   **R. Gubó**, C. M. Yim, M. Allan, C. L. Pang, A. Berkó, G. Thornton; *Variation of SMSI with the Au:Pd Ratio of Bimetallic Nanoparticles on TiO$_2$(110);* TOPICS IN CATALYSIS (2018)
IF=2.486; MTMT [3317282]

PhD03.   P. Mutombo, **R. Gubó**, A. Berkó; *Interaction of Gold with a Pinwheel TiO$_{\sim1.2}$ Film Formed on Rh(111) Facet: STM and DFT Studies;* JOURNAL OF PHYSICAL CHEMISTRY C 120:(23) pp. 12917-12923. (2016)
IF: 4.536; MTMT [3110742]

PhD04.   L. Óvári, A. Berkó, G. Vári, **R. Gubó**, A. P. Farkas, Z. Kónya; *The growth and thermal properties of Au deposited on Rh(111): formation of ordered surface alloy;* PHISICAL CHEMISTRY CHEMICAL PHYSICS (PCCP) 18: pp. 25230-25240. (2016)
IF: 4.123; MTMT [3101262]

PhD05.   **R. Gubó**, L- Óvári, Z. Kónya, A. Berkó; *Growth of Gold on a Pinwheel TiO$_{\sim1.2}$ Encapsulation Film Prepared on Rhodium Nanocrystallites;* LANGMUIR 30:(48) pp. 14545-14554. (2014)
IF: 3.833; MTMT [2783054]

PhD06.   L. Óvári, A. Berkó, **R. Gubó**, Á. Rácz, Z. Kónya; *Effect of a Gold Cover Layer on the Encapsulation of Rhodium by Titanium Oxides on Titanium Dioxide(110);* JOURNAL OF PHYSICAL CHEMISTRY C 118:(23) pp. 12340-12352. (2014)
IF: 4.536; MTMT [2602099]

$\sum$IF = 24,05

OTHER PUBLICATIONS

1. Á. Szitás, **R. Gubó**, T. Pásztor, A. P. Farkas, T. Ajtai, L. Óvári, K. Palotás, A. Berkó, Z. Kónya; *Adsorption of Azobenzene on Hexagonal Boron Nitride Nanomesh Supported by Rh(111);* JOURNAL OF PHYSICAL CHEMISTRY – accepted for publication (2020); IF: 4.536

2. **R. Gubó**, M. Lukovics, N. Nádasi; *A junior kutatók felelősségteljes innováció iránti fogékonyságának vizsgálata eltérő innovációs környezetben;* TÉR-GAZDASÁG-EMBER, A Széchenyi István Egyetem Gazdaságtudományi Karának tudományos folyóirata (2019); ISSN: 20564-1176

3. **R. Gubó**, G. Vári, J. Kiss, A. P. Farkas, L. Óvári, A. Berkó, Z. Kónya; *Tailoring the hexagonal boron nitride nanomesh on Rh(111) by gold;* PHISICAL CHEMISTRY CHEMICAL PHYSICS (2018) IF: 4.123; MTMT [3368595]

4. A. P. Farkas, Á. Szitás, G. Vári, **R. Gubó**, L. Óvári, A. Berkó, J. Kiss, Z. Kónya; *Effect of Gold on the Adsorption Properties of Acetaldehyde on Clean and h-BN Covered Rh(111) Surface;* TOPICS IN CATALYSIS (2018) IF=2.486; MTMT [3370969]

5. A. Berkó, **R. Gubó**, L. Óvári, Z. Kónya; *Rh and Au deposited on ultrathin $TiO_{\sim1.2}$ film formed on Rh(111) facets and the effects of CO exposure;* SURFACE SCIENCE 641: pp. 300-304. (2015) IF: 2.060; MTMT [2857963]

6. A. Berkó, **R. Gubó**, L. Óvári, L. Bugyi, I. Szenti, Z. Kónya *Interaction of Rh with Rh nanoparticles encapsulated by ordered ultrathin TiO_{1+x} film on $TiO_2(110)$ surface;* LANGMUIR 29:(51) pp. 15868-15877. (2013) IF: 3.833; MTMT [2491344]

$\sum IF = 41,086$

PRESENTATIONS AT INTERNATIONAL AND HOME CONFERENCES

i. **R. Gubó**, G. Vári, J. Kiss, A. P. Farkas, L. Óvári, A. Berkó, Z. Kónya: *Tailoring the hexagonal boron nitride nanomesh on Rh(111) by gold;* ECOSS34 Aarhus, Denmark, 2018. August 27-31 – oral presentation

ii. **R. Gubó**, C. M. Yim, M. Allan, C. L. Pang, L. Óvári, A. Berkó, G. Thornton: *Comparison of thermally induced material transport processes and resistance against TiO_x decoration of Au-Pd and Au-Rh double films on TiO2(110) surface;* ECOSS33 Szeged, Hungary 2017 August 27 – September 1 – poster presentation

iii. P. Mutombo, **R.Gubó**, A. Berkó: *Interaction of gold with a pinwheel TiO~1.2 film formed on Rh(111) facets: STM and DFT studies;* ACSIN-13 Rome, Italy 2016 October 9-15 – poster presentation (co-author)

iv. **R. Gubó**, L. Óvári, Z. Kónya, A. Berkó: *STM-study of 1D interface between Au and $TiO_{~1.2}$ monolayers formed on Rh(111) facets of Rh particles supported by $TiO_2(110)$;* JVC-15 Wien, Austria 2014 – poster presentation

v. **R. Gubó**, A. Berkó: *Rh adszorpció ultravékony (<0.3 nm) TiO_x filmmel bevont Rh(111) felületen: STM vizsgálatok,* Magyar SPM találkozó VIII. Debrecen, Hungary 2013 – oral presentation

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