Final report on the OTKA project K81660

‘Fabrication and spectroscopic characterization of well defined low-dimensional surface structures’

The project was directed to the investigation of 0D, 1D and 2D metallic and non-metallic nano-objects to enhance the efficiency of platinum metal heterogeneous catalysts or to replace them by cheaper but still active catalysts. Emphasis was put on studying the effect of modifiers on catalytic properties. Among them, gold, molybdenum, potassium, boron and atomically thin TiO_X, CeO_X and MoO_X layers were used. Ultrathin oxide layers are gaining great scientific and technological interest, because they can serve as templates for particle growth, modifiers in catalysis **[1]**, insulators in metal-insulator-metal electronic components, and so on. Beside catalysis, the study of well-defined 2D surface structures is related to the production of electric energy with high efficiency from light by the so-called rectifying antennas or rectennas **[2]**. This approach, although technologically is challenging, represents an alternative way of light energy harvesting to conventional solar cells and deserves attention at the present developed stage of nanosciences.

The applied methods were X-ray photoelectron spectroscopy (XPS), Reflection Absorption Infrared Spectroscopy (RAIRS), Thermal Desorption Spectroscopy (TDS), low energy ion scattering spectroscopy (LEIS), Auger Electron Spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and work function (WF) measurements.

The results of our investigations acknowledged to the project have been published in 16 international journals, with a sum of impact factors 49.18 and were also presented in 3 posters and 25 talks, among which 5 were invited lectures. Owing to the support of the project, one accepted talk will be given and 3 more publications are to be submitted in the next half year.

The staff taking part in the project had some changes, two Phd students left the team but two Phd students attached to it. The Reaction Kinetics Research Laboratory in the meantime disjoined from the Chemical Research Center, changed name to MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group and joined TKI, also belonging to the Hungarian Academy of Sciences. Due to renovation of the university building giving home to the group, we had to move twice with all the apparatus during the project time, hence the fulfillment of project was hindered and it was prolonged by one year. We installed a new apparatus, a Besocke type Kelvin-probe owing to the support from the project, which helps collecting work function data with high sensitivity in a continuous way. According to the suggestion of OTKA committee, we focused our work on a few major directions. Besides investigating bimetallic systems, we put emphasis on studying atomically thin oxide layers, including metal-oxide-metal (MOM) structures, which have great importance in catalysis **[1]** and nanoelectronic devices. MOM tunneling diodes can be applied in a nano-sized rectenna **[2]** for rectifying at optical frequencies**,** making possible in principle the generation of electricity from sunlight with high efficiency. We have characterized a graphene-analogous 2D material, boron nitride, which shows promising electronic and structural properties **[3]**. In the frame of an argentine cooperation, computer simulation works were done to elucidate the effect of alkali promoter on a catalytically active transition metal carbide, which can replace platinum metal catalysts and shows high tolerance towards sulfur-containing catalyst poisons. Experimental and theoretical works were also performed in bilateral cooperation with French, German and Czech researchers.

One part of the project is attached to the effect of a second metal on the structure, stability and activity of metal catalyst particles. Among the applied metals were molybdenum and gold, the former is being a cheap, but efficient promoter or support material, while the latter shows extreme catalytic activity when nano-sized. To test the catalytic activity, studying the surface reactions of CO was chosen.

The properties of separate Mo particles were addressed on a titania support [4]. Tunneling induced decomposition of $Mo(CO)_6$ from the gas phase was studied on $TiO_2(110)$ surface by STM and STS. The efficiency of the procedure was followed by measuring the dot volume as a proportional indicator of the amount of the decomposed precursor. It was found that below $1*10^{-5}$ Pa background pressure of $Mo(CO)_6$, there is no measurable effect and above $1*10^{-4}$ Pa, the nanodot size is too large compared to the curvature of the tip (20-40 nm). A threshold bias of +3.1(+/-0.1) V on the sample was measured for the decomposition of $Mo(CO)_6$ in gas ambient. In the absence of the precursor, dot formation was observed only above +3.7(+/-0.2) V, in good agreement with the results reported in our earlier work about nanolithography on clean $TiO_2(110)$ substrate (E. Kriván,A. Berkó:J. Vac. Sci. & Tech. B15(1) (1997) 25). By applying voltages in the range of 3.1-3.5 V, a systematic enlargement of the created nanodots was found in the range of 2-20 s of duration and 0.01-1.0 nA of tunneling current. The I-V curves detected on the top of the nanodots have shown that the created features are of insulator character. This observation indicates that the decomposition of $Mo(CO)_6$ is also accompanied by oxidation of the deposited Mo species.

The structural and chemical characterization of Rh, Mo and Rh–Mo nanosized clusters formed by physical vapor deposition on TiO_2 single crystal was performed by AES, TDS and RAIRS, applying CO as test molecule [5]. On a slightly reduced titania surface 2D-like growth of Rh was revealed at 300 K up to 0.23 ML coverage by AES and CO-desorption experiments. For CO-saturated Rh particles TDS showed molecular CO desorption in a broad temperature range with T_p=400, 440, 490 and 540 K (α-states), the latter state appearing only on the smallest Rh particles. The population of γ-state (T_p=780–820 K) originating from the recombination of C and O atoms on the support began at Θ_{Rh}=0.23ML and was maximized at around 1–2 ML Rh coverage, corresponding to 30% dissociation of CO. A possible dissociation precursor on Rh particles is identified as linearly bonded CO on step sites characterized by ν(C–O) of 2017 cm^{-1}. Deliberation of CO_2 could not be detected between 170 and 900 K, showing the absence of disproportionation reaction. Instead of oxidizing CO molecules, oxygen atoms stemming from the dissociation of CO attached to the reduced centers of titania, indicating the role of adsorption sites at the perimeter of Rh particles in the decomposition process. 2 ML of predeposited Mo enhanced markedly the dispersion of Rh particles as a result of strong Rh–Mo interaction, but it slightly reduced the molecular α-CO desorption possibly due to enhanced dissociation. The formation of γ-CO was suppressed considerably through elimination of adsorption centers by Mo on the TiO_2 substrate. The reactivity of Rh layers deposited on Mo-covered surface towards CO was reduced after repeated annealing to 600 K due to partial encapsulation of Rh by titania, manifesting in the suppression of the more strongly bonded α-state. Mo-deposits (up to 0.5 ML) on Rh particles decreased the saturation coverage of α-CO through a site-blocking mechanism without detectable influence on the binding energy of CO to Rh, indicating Mo island formation. The carbon arising from the decomposition of CO dissolved in the Mo containing particles formed a solid solution stable even at 900 K, suggesting a possible role of molybdenum carbide regarding the enhanced catalytic activity of Rh clusters.

For model studies of well-defined metal clusters, the structure of support must be single-crystalline to act as a template for controlled particle-growth. Beside TiO_2 single crystal, 1D titanate structures were also applied as support materials of Rh and Rh-Au particles. A critical issue, the effect of adsorbed gas on the bimetallic structures was also addressed.

Gold, rhodium and their coadsorbed layers were prepared on titanate nanowires and nanotubes and characterized by XPS, LEIS, FTIR and SEM [6]. On titanate nanowire and tube supports the gold $4f_{7/2}$ XP emission appeared after reduction at 83.7 eV and 85.6 eV indicating two different sizes or chemical environments of gold nanoclusters. The titanate nanostructures stabilize the nearly atomically dispersed state of gold (85.6 eV peaks in XPS). Small clusters also developed in rhodium containing samples besides the pure metallic state. Upon CO adsorption on Rh/titanate nanostructures the IR stretching frequencies characteristic of twin form were dominant, whereas bimetallic nanosystems featured a pronounced linear stretching vibration. By performing careful XPS, LEIS and SEM experiments, it was found that, for appropriate Au and Rh coverage, the Au almost completely covers the Rh nanoparticles. CO adsorbed on this surface may induce surface reconstruction.

Au, Rh, and Au-Rh clusters were studied on Al_2O_3, TiO_2 powders and titania nanowire **[7]** by XPS, SEM and FTIR. On the XP spectra of the Au-Rh/TiO_2 and Au-Rh/Al_2O_3 powders and wires the binding energy of the Au 4f emission was practically unaffected by the presence of Rh, the position of Rh 3d remained also constant on alumina, while it shifted to lower binding energy with gold admixture on titania. New emission for Rh 3d at 309.2 eV and for Au 4f at 85.6 eV developed on titania wire case. The bands due to Rho-CO and $(Rho)_2$-CO were observed on IR spectra of titania supported bimetallic samples. The peak due to Rh^+-$(CO)_2$ was less intense on bimetallic nanowire. All three bands however are intense on Au-Rh/Al_2O_3. The results were interpreted by electron donation from titania through gold to rhodium. “Core-shell” bimetallic structures are supposed on Au-Rh/titania wire.

Beside Mo and Au, potassium was also applied as a second metal to modify the properties of Rh nanoparticles. K is known as a promoter in heterogeneous catalysis, but its effect on the structure and reactions of Rh clusters supported by titania has been scarcely studied.

The deposition of potassium onto $TiO_2(110)$ surface at 330 K and the effects of post-annealing were investigated by STM, TDS and AES [8]. At lower K coverages (a few percentage of a monolayer), 3–4 nm long and 1–2 nm wide islands appear which can be identified with K covered regions. At higher K coverages the surface exhibits disordered structures. Depending on the initial K coverage, the annealing above 700 K in UHV results in ordering of the surface. For app. 1/3 monolayer K and annealing at around 900 K, the entire surface reconstructs into a (1×2) phase accompanied by the appearance of pits with an average diameter of 20–30 nm. This morphology is characteristic up to 1000 K. Above this temperature, the recovery of the (1×1) phase was observed. At low K coverages (<0.2 ML) the annealing at 1000 K resulted in the formation of protruding islands of approximately 2×2 nm2 which were identified with a strongly bonded surface compound containing K.

In order to understand the promoting mechanism of alkali additives, we have studied potassium overlayers on $TiO_2(110)$ [9]. The surface was prepared by thermal segregation of K from the bulk to the surface above 750–800 K. The bulk diffusion of the Ti/O ions is required for the migration of large K ions inside the lattice. STM and LEIS revealed that segregated potassium forms small clusters of 1–2 nm on the surface, containing also oxygen. These clusters are located preferentially on the one-dimensional defect sites (Ti_2O_3 strings) of the (1x1) rutile surface and on the Ti_2O_3 rows of the (1x n) reconstructed surfaces. According to XPS, the potassium on the surface after segregation at 1000 K is only partially ionized and the Ti 2p region is dominated by the Ti^{4+} component. XPS and LEIS provided evidence of a very clear preference for the Rh clusters to grow near 300 K not on the potassium structures but on the potassium free parts of titania surface. This finding may imply the absence of a direct contact between Rh and K at low Rh coverages. Nevertheless, evaporation of Rh on $K/TiO_2(110)$ results in more cationic K sites, due to an electron transfer from K to Rh through titania. The decoration and encapsulation of Rh nanoparticles by TiO_x proceed also in the presence of potassium. The capping layer does not contain potassium. At large Rh cluster sizes, the wheel-like structure of the cover layer could be identified with a structure found on top of Rh crystallites formed on the K-free titania surface. The presence of potassium stabilized CO on Rh nanoparticles, which is attributed to the indirect charge transfer from potassium structures to rhodium (long range effect).

The influence of alkali additive on the bonding of CO was addressed by computer simulation study on Mo_2C, which is a promising substitute for platinum metal catalysts [10].

We studied the effect of K on the adsorption and dissociation of CO on the β-$Mo_2C(001)$ surface by density functional theory calculations. Molecular CO adsorbs more strongly on Mo-terminated surfaces than on C-terminated ones. Adsorption is energetically more favorable in the presence of preadsorbed potassium. The CO molecule withdraws electron density from the surface, being more extended on the K-doped surface. The CO dissociation was also evaluated, and reaction pathways were modeled, revealing that the C-terminated surface is energetically less favorable than the Mo-terminated one. For both surfaces, the activation energy barrier for dissociation increases with the K content. C-O vibrational frequencies were also computed on K-modified surfaces.

Atomically thin oxide layers have unique properties, great scientific and technological importance [1]. We prepared TiO_x and MoO_x overlayers on Rh nanoparticles and continuous films formed on $TiO_2(110)$ single crystal and characterized their structural and chemical properties. On well-ordered TiO_x encapsulation layers Rh deposits were formed and their structure, reactivity and the circumstances for the production of intact metal-oxide-metal structures were determined. The formation of ultrathin CeO_x films on Cu(111) and the reactions of Co overlayers deposited on this substrate has also been studying.

Rh nanoparticles of 20-40 nm lateral size were grown on $TiO_2(110)$ surface by physical vapor deposition and thermal treatments [11]. The top-facet morphology of the Rh nanoparticles and the particle-free support were characterized by STM. The chemical composition of the surface was checked by AES. Although most of the particles exhibited complex overlayers, ordered decoration layers were detected only on the top facet of extended hexagonal Rh particles. Several ordered or quasi-ordered encapsulation phases were detected: (1) a “worm-like” overlayer consisting of 1D stripes (width of 0.5 nm and length of 2-3nm) oriented in the close-packed crystallographic orientations of the Rh nanoparticles and (2) a “wheel-like” hexagonal structure with unit cell vectors of 1.50+-0.05 nm. The “worm-like” structure is suggested to be an initial stage in the formation of a “wheel-like” structure. It was proved that it is possible to selectively remove the “wheel-like” decoration phase by Ar^+ sputtering and to recover it by thermal treatment of a few minutes at 1000 K.

Rh films of 5−50 monolayers (ML) were grown on $TiO_2(110)-(1\times1)$ surface by physical vapor deposition (PVD) at 300 K followed by annealing at max. 1050 K [12]. In the coverage range of 5−15 ML, separated stripe-like Rh nanoparticles of approximately 30×150 nm lateral size and 10−20 layer thickness with a flat top (111) facet were formed. At higher coverages (15−50 ML), the Rh film sustained its continuity at least up to 950 K. For both cases, the Rh(111) top facets were completely covered by a long-range ordered hexagonal “wagon-wheel” TiO_{1+x} ultrathin oxide (hw-TiO-UTO) film. STM-STS, XPS, LEIS, and TDS methods were used for morphologic and electronic characterization of surfaces prepared in this way. The main part of this study is devoted to the study of postdeposition of Rh on the hw-TiO-UTO layer at different temperatures (230 K, 310 K, 500 K) and to the effect of subsequent annealing. It was found that 2D nanoparticles of 0.2−0.3 nm height and 1−2 nm diameter are formed at RT and their average lateral size increases gradually in the range of 300−900 K. The LEIS intensity data and the CO TDS titration of the particles have shown that an exchange of the postdeposited Rh atoms with the hw-TiO-UTO layer proceeds to an extent of around 50% at 230 K and this value increases up to 80−90% in the range of 300−500 K. The total disappearance of the characteristic LEIS signal for Rh takes place at around 900 K where a complete hw-TiO-UTO adlayer forms on top of the postdeposited metal (100% exchange).

Rh overlayers formed on slightly oxygen deficient TiO_2(110) single crystals, as well as on ultrathin encapsulation titania layers prepared on Rh multilayers were characterized by AES, LEIS, XPS, TPD and WF measurements [13]. Rh deposition on TiO_2(110) below 0.1 monolayer (ML) Rh coverage led to electron transfer from the metal toward the TiO_2(110) surface. Annealing of Rh multilayers up to 950 K in UHV resulted in the surface diffusion of titanium and oxygen ions into a TiO_x encapsulation layer of definite stoichiometry and a thickness of a few atomic layers. The accompanying 0.3–0.6 eV WF enhancement at Θ_{Rh}=2–6 ML can be attributed to the smoothing of the Rh overlayer and the formation of a continuous TiO_x dipole layer consisting of positively charged titanium ions at the metal–oxide interface and negative oxygen ions in the topmost layer. De-encapsulation of Rh particles was observed on a TiO_2 sample less reduced in its bulk, revealing the roles of bulk and surface substrate stoichiometry on the decoration process. Increasing the thickness of Rh multilayers supported on the TiO_2(110) single crystal hampered ion diffusion and consequently, it led to an increase in the temperature characteristic of the completion of the encapsulation. Deposition of additional Rh on the TiO_x encapsulation layers covering Rh multilayers resulted in the growth of Rh particles having a similar height up to 1 ML. LEIS data indicated that the decoration of the second metal layer by titania was hindered. It occurred at a temperature more than 100 K higher than that characteristic of the TiO_2(110) surface at the same Rh coverage. Aspects of the produced structures in relation to the formation of protective oxide layers, modification of surface work function, catalysis and metal–insulator–metal (MIM) devices are important.

We have established the catalytic activity of TiO_x modified Rh films, representing inverse model catalysts. We have verified in a UHV model study that the maximum hydrogenation rate of CO found on Rh at around 0.2 ML TiO_x coverage in high pressure studies is related to the dissociation of CO.

The effect of TiO_x on the bonding of CO test molecule to different Rh surfaces has been investigated in model systems under UHV conditions [14]. The TiO_x overlayers had a twofold effect both on Rh nanoparticles and Ar+-ion sputtered Rh films prepared on TiO_2(110). They suppressed the uptake of molecular CO by a site blocking mechanism. In the other mechanism the recombinative CO desorption states went through a maximum at intermediate TiO_x coverages on both kinds of rhodium surfaces, indicating the promotion of CO decomposition. These findings are in harmony with earlier high pressure studies which showed that the methanation rate of CO on rhodium is maximal at intermediate TiO_x coverages. The effect of a TiO_x film underneath a Rh deposit (0.4monolayer) on its surface chemistry has also been addressed. A Rh-TiO_x-Rh structure was formed at 230 K by the deposition of Rh on a continuous TiOX film supported by a 20 monolayer thick Rh multilayer. CO desorption curves indicated a highly reactive Rh overlayer at 230 K and also a dramatic structural change in the rather narrow temperature range of 230-265 K. The rearrangement is accompanied by the migration of TiO_x species onto the postdeposited Rh as it can be deduced from the appearance of a CO desorption feature with T_p=360 K. The driving force of the process is the formation of strong Rh-Rh bonds and the low surface free energy of TiO_x overlayer with respect to the bare Rh surface.

The proceeding of the encapsulation process, that is the decoration of Rh deposits by TiO_x overlayer, can be influenced by the presence of a second metal. Beside the effect of potassium and molybdenum, the impact of co-deposited gold was also investigated.

Our study focuses on the thermal behavior of continuous rhodium thin films (~10 nm) deposited on a TiO_2(110) substrate at 300 K and covered by a continuous ultrathin gold film (~1 nm), applying STM, XPS, and LEIS techniques [15]. This arrangement facilitated a rather clear-cut investigation into the effect of the Au cover layer on the well-known encapsulation/decoration of Rh by TiO_x, since the contribution of the titania substrate to the XPS and LEIS spectra could be avoided. Upon annealing a monometallic Rh film, the diffusion of Ti and O from the TiO_2(110) substrate on top of the Rh film is essentially complete up to 850 K, leading characteristically to the formation of a “pinwheel” encapsulation layer with a $TiO_{1.2}$ stoichiometry. The dewetting of the Rh film does not take place up to 950 K. Upon annealing of the Rh film in the presence of a continuous Au cover layer, the diffusion/accumulation of O was completely blocked up to 850 K, but metallic Ti was well detectable by XPS. Since LEIS spectra were dominated by the Au peak, and almost no Ti signal was observable up to this temperature, the metallic Ti is mainly stabilized at subsurface positions, probably either at the Rh−Au interface or within the Au film, in any case in contact with Au. The complete separation of O and Ti diffusion in this temperature range can be attributed to the weak interaction between oxygen and gold. Raising the sample temperature up to 930 K induces substantial changes. The diffusion of O is no longer kinetically hindered, and it reacts with a part of the alloyed Ti to form well-separated TiO_2 nanoclusters on top of the Au shell. However, no oxygen is stabilized at subsurface sites in the bimetallic film. The rest of Ti alloyed in the subsurface is detectable by STM as ringlike features. The “pinwheel” $TiO_{1.2}$ encapsulation layer appearing typically on a pure Rh film did not form on the bimetallic Au−Rh film at any of the temperatures investigated.

We have characterized a graphene-analogous 2D material, boron nitride [3], which shows promising electronic and structural properties.

The segregation of boron and its reactivity toward nitric oxide have been investigated by means of high resolution AES, XPS, TDS and UPS [16]. The segregation of boron from a Rh foil started from 700 K. Its presence altered the surface behaviors of Rh; the uptake of NO increased by about 30–37%. Whereas the dissociation of NO was about 3–10% on a clean, boron-free surface, the extent of dissociation (at saturation) at highest boron level was almost 98%. This feature strongly suggest a direct interaction between NO and boron on the surface. The presence of boron greatly stabilized the adsorbed nitrogen and oxygen formed in NO dissociation. Boron oxide (BO, B_2O_2) sublimated from the surface below 1000 K.

Clean, single BN layer formed on the surface close to a monolayer regime, presumable in nanomesh structure.

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