

Characterization of catalyst surfaces by X-ray photoelectron spectroscopy

Thesis of the PhD dissertation

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1 Introduction

It is obvious that some atomic layers of solid surfaces strongly determine the physical and chemical properties of the material. Therefore, if we want to understand the nature of heterogeneous chemical processes, we must have recourse to techniques which provide us information about these very narrow regions. The development of these surface analytical methods have enhanced in the middle of the last century having led to our modern ion- and electron spectroscopies where the two flagships of them are the Auger electron spectroscopy (AES) and the X-ray photoelectron spectroscopy (XPS). Before the seventies the number of publications on XPS and AES had been approximately equal, after 1985 XPS became much more dominant. Both methods are characterized by easy elemental identification and detection of chemical environments, while they are principally nondestructive. As electron beams can be focused on a very small probe size, excellent spatial resolution can be achieved, thus the examination of small sample surfaces have become available. XPS collects informations from significantly wider area but a higher energy-resolution enables it to map the elements and the chemical states in a more efficient and more reliable way than AES does. Both spectroscopies can be easily combined with ion sputtering to obtain high-resolution compositional depth profiles so the bulk composition will not be hidden from us in case of necessity. The low energy ion scattering spectroscopy reckons among a relatively young technique which give us information about the topmost surface layer. In this case we can determine the energy distribution of backscattered low energy ions after impact against the investigated surface. These informations allow us to conclude the weights of atoms that compose our sample. Beyond quantification, also qualitative information can be extracted by LEIS but we have to maintain the same operation parameters on every occasion of taking spectra.

The X-ray photoelectron spectroscopy can be discussed by means of concepts used in information theory as well. Our samples, may be called source, carry some pieces of information with maximum uncertainty and entropy in the beginning. We can say that we possess some negative information so the measurements are aimed at canceling this uncertainty. There is no sense in considering information until we define the appropriate probability field we wish to investigate. In our case this is the binding energy of electron levels at surface atomic layers which are in relation to chemical environment, oxidation state at the same time. The interpretation of measurement can be treated like we put a question to the system and afterward observing its answer in the form of measuring the kinetic energy of the emitted photoelectrons. If we bear energy of photons in mind as a well defined quantity we make some approximations actually, because we have to treat this energy as a random variable instead of a deterministic signal whose maximum value is 1486.6 eV in the case of Al and 1253.6 eV for Mg anode but there are some other possible values with lower probability contributing satellite peaks of the photoelectron spectra. In the progress of measurements we are gaining more and more pieces of information, the initial uncertainty or entropy of the system keeps diminishing. In the course of decoding

process we must realize the disturbing presence of a certain amount of bits, noises which are added to our signals and we have to minimize the contributions of them. For the sake of decreasing the distortion effects of the noise we must use ultrahigh vacuum but the entire elimination of them is not possible because there are electrons from deeper layer regions which sustain different order of energy loss. This effect can be decreased by increasing the surface sensitivity when we expand the angle defined by the surface normal of the sample and the incident X-ray beam. In our case there is a bijection between the kinetic and binding energy of electrons. In other words we can deal with unambiguously decodable series of signals. Taking a spectrum means mapping the determined binding energy values to the set of intensity values. However, we must face up to further difficulties due to overlapping of the spectra. In order to cope with this problem we can deconvolute the initial spectra into synthetic components. The criteria of one-to-one mapping is not granted in this case because a given series of peaks yield only one result but one can divide the resultant spectrum into components in various ways which sometimes prove to be a difficult task (Ce 3d spectra for example).

On the one hand we have sought answers through measurements to characterize the physical and chemical features of one- and bimetallic systems of gold and rhodium which is formed on the surface of titanate nanotube and nanowire supports. On the other hand further aim was to explain the activity change of samples in the course of catalytic reactions and reveal the modification in surface composition. Two catalysts were investigated in different reactions, while we inquired about

1. the interaction between rhodium and vanadium on Rh/10% V₂O₅-Al₂O₃ catalyst which produce detectable changes in the CH₄+CO₂ reaction
2. the modification of oxidation state in metallic state copper on multiwall carbon nanotube support in the CH₃OH+CO+O₂ reaction and this can be any connection with catalytic activity.

2 Experimental and methods of the evaluation

XP spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical analyzer and nine channeltrons. The analyzer was operated in the FAT mode with 20 eV pass energy. Electrons were collected for 100 ms in one channel and 5-10 scans were summed to get a single high resolution spectrum so as to improve signal/noise ratio.

In every case the pressure in the analyzing chamber was smaller than 10⁻⁸ mbar. The pump system was oil-free in order to avoid contaminating our samples by outer carbon species. The pressure was monitored by Bayard-Alpert gauges in every separated spaces of the XPS.

The Al K_α (hν=1486.6 eV) and the Mg K_α (hν=1253.6 eV) non monochromatic radiation of a dual anode X-ray gun (XR50) was used as an excitation source. The gun was operated at the power of 150 W (12.5 kV, 12 mA).

Our samples were pretreated in a high pressure cell directly attached to the analyzing chamber where we could set up almost the same reaction conditions as others had used in the course of kinetic studies. We applied electron bombardment sample heating in the high pressure cell with the help of an Euroterm 2208 control unit.

A SPECS IQE 12/28 ion source was used for generation of low-energy ion scattering spectra, while the analyzer was operated in the FRR mode. Helium ions of 800 eV kinetic energy were applied at low ion flux, which was necessary to avoid the sputtering of surface. The incident angle was 55° (with respect to surface normal), ions ejected along the surface normal were detected.

For data acquisition and evaluation both manufacturer's (Specslab2) and commercial (CasaXPS, Origin 8.0) software packages were used.

3 New scientific results

I. *The surface of titanate nanotube and nanowire supports is able to stabilize gold and rhodium nanosized noble metal clusters after reduction [1,2].*

In the case of 1% Au/TiO₂ nanowires two peaks are observed on the reduced sample for Au 4f peaks where the component with smaller binding energy is attributed to metallic state and the other peak has a connection with gold atoms in very small sized nanoparticles. On 1% Au/TiO₂ nanotubes the intensity of the atomically dispersed gold is less than on wire. From these observations we have concluded that nanowire can stabilize very small sized gold nanoparticles more efficiently than nanotubes do. After reduction on 1 w% Rh/TiO₂ nanowires the deconvolution of Rh 3d spectra also reveals a dominant peak for metallic state rhodium and a smaller component of more dispersed rhodium clusters. We cannot observe the presence of nanosized particles for rhodium on nanotubes which indicates the difference in the surface structure of these oxid supports.

Also on bimetallic nanowires and nanotubes gold and rhodium nanoclusters exist but there is a significant decrease in their XP signal intensity. These results prove the enlargement of nanoclusters on bimetallic systems compared to monometallic systems.

II. *Core-shell gold, rhodium bimetallic systems are formed on the reduced titanate nanotube and nanowire supports whose sizes and structures depend on the reaction types [6,4,5].*

Due to surface diffusion gold atoms are able to fully or partially cover rhodium particles depending on their concentration ratios. The thermodynamical driving force may be the decrease of surface energy. The transport process leads to the formation of core-shell structure with gold atoms in the outer and rhodium atoms in the inner regions. This statement are supported by our LEIS studies. In the case of 0.5% Au + 0.5% Rh bimetallic

nanocomposites the rhodium peak does not separate from noise level, only the gold signal shows up. In the bimetallic system the LEIS intensity of gold is substantially higher than in the monometallic case which indicates increased amount of gold atoms on the surface. Carbon monoxide adsorption induces the disruption of rhodium to smaller clusters on bimetallic titanate nanowire.

Increase in the size of bimetallic clusters on 0.5% Au + 0.5% Rh TiO₂ nanowire can be observed during hydrogenation of carbon dioxide. The XP signals of small rhodium and gold particles can also be identified before the reaction. The gold spectra is unchanged throughout the reaction but the intensity of nanosized rhodium keeps diminishing and nearly completely vanishes after 60 min of the CO₂+H₂ reaction. The observable difference between the XP spectra can be attributed to agglomeration processes.

III. *The oxidation of metallic state copper occurs in the oxycarbonylation of methanol on multiwall carbon nanotubes [9].*

In the Cu 2p spectra taken after reduction of catalyst, there is no sign of the satellite structures that would be the result of the formation of metallic state copper. The value of Auger parameter supports this statement as well. Significant Cu LMM peak shift toward smaller kinetic energy can be seen after hydrogen treatment of the samples while growing intensity of the satellite signals follows the Cu 2p spectra during the reaction. Considering the fact that Cu⁺ ions do not contribute to any satellite structure we conclude that the CH₃OH+CO+O₂ reaction brings about the oxidation of copper which is mostly in the Cu⁺ state, with some Cu²⁺ also present on the surface. We have reached the conclusion that the increased activity has occurred in kinetic measurements is closely connected with the surface concentration of oxidized Cu.

IV. *The higher catalytic activity of Rh/V₂O₅-Al₂O₃ catalyst in the CH₄+CO₂ reaction is associated with the presence of V⁴⁺ [3].*

Three catalysts are involved in the investigation of the CH₄+CO₂ reaction: Rh/Al₂O₃, Rh/TiO₂-Al₂O₃ and Rh/V₂O₅-Al₂O₃. Comparing the hydrogen and the CO formation rate related to the number of surface metal atoms we can conclude that the activity of Rh/V₂O₅-Al₂O₃ is higher than that of Rh/TiO₂-Al₂O₃. At 773 K we cannot see any significant difference between the three samples in the decomposition rate of CH₄. During the reaction the positions and the intensities of Rh 3d peaks are unaltered corresponding to metallic state. The binding energy of Ti 2p electrons in the Rh/TiO₂-Al₂O₃ shifts only few tenths eV downwards after the reduction of the catalyst, but does not change further. XPS results have revealed the presence of V⁴⁺ and V⁵⁺ after reduction on catalyst promoted with V₂O₅. At 773 K the reduction of vanadium is evoked by hydrogen that is activated on rhodium. The increase in conversion observed on V₂O₅ promoted Rh/Al₂O₃ catalysts

may be attributed to the V^{+4} which facilitates the dissociation of carbon dioxide.

4 Practical application of the results

We have pointed out that nanostructured titanates can stabilize metal nanoparticles on their surface. This property makes the usage of TiO_2 nanowires and nanotubes possible as oxid supports in catalytic reactions. We have successfully explained the reasons of kinetic characteristic in the investigated reactions. These results may prove to be a really useful informations for designing new and more effective catalysts in the future.

5 Publications related to the thesis

1. Kukovecz, Á; Pótári, G; Oszkó, A; Kónya, Z; Erdőhelyi, A; Kiss, J,
Probing the interaction of Au, Rh and bimetallic Au-Rh clusters with the TiO₂ nanowire and nanotube support
Surface Science, **605**, 1048-1055 (2011). (IF=1.838)
2. Oszkó, A; Pótári, G; Erdőhelyi, A; Kukovecz, A; Kónya, Z; Kiricsi, I; Kiss, J,
Structure of the Au-Rh bimetallic system formed on titanate nanowires and nanotubes
Vacuum, **85**, 1114-1119 (2011). (IF=1.530)
3. Sarusi, I; Fodor, K; Baán, K; Oszkó, A; Pótári, G; Erdőhelyi, A,
CO₂ reforming of CH₄ on doped Rh/Al₂O₃ catalysts
Catalysis Today, **171**, 132-139 (2011). (IF=2.980)
4. Kiss, J; Oszkó, A; Pótári, G; Erdőhelyi, A,
Role of the nature of support on the structure of Au-Rh bimetallic nanoparticles
Vacuum, **86**, 594-598 (2012). (IF=1.530)
5. Kiss, J; Óvári, L; Oszkó, A; Pótári, G; Tóth, M; Baán, K; Erdőhelyi, A,
Structure and reactivity of Au-Rh bimetallic clusters on titanate nanowires, nanotubes and TiO₂(110)
Catalysis Today, **181**, 163-170 (2012). (IF=2.980)
6. Tóth, M; Kiss, J; Oszkó, A; Pótári, G; László, B; Erdőhelyi, A,
Hydrogenation of carbon dioxide on Rh, Au and Au-Rh bimetallic clusters supported on titanate nanotubes, nanowires and TiO₂
Topics in Catalysis, **55**, 747-756 (2012). (IF=2.608)
7. Madarász, D; Pótári, G; Sápi, A; László, B; Csudai, C; Oszkó, A; Kukovecz, A;
Erdőhelyi, A; Kónya, Z; Kiss, J,
Metal loading determines the stabilization pathway for Co²⁺ in titanate nanowires: ion exchanges vs. cluster formation
Physical Chemistry Chemical Physics, **15**, 15917-15925 (2013). (IF=3.829)
8. Pótári, G; Madarász, D; Nagy, L; László, B; Sápi, A; Oszkó, A; Kukovecz, A;
Erdőhelyi, A; Kónya, Z; Kiss, J,
Rh-induced support transformation phenomena in titanate nanowire and nanotube catalysts
Langmuir, **29**, 3061-3072 (2013). (IF=4.187)

9. Merza, G; László, B; Oszkó, A; Pótári, G; Baán, K; Erdőhelyi, A,
The direct synthesis of dimethyl carbonate by the oxycarbonylation of methanol over Cu supported on carbon nanotube
(submitted)

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6 Publications not related to the dissertation

1. Veres, A; Ménesi, J; Juhász, A; Berkesi, O; Ábrahám, N; Bohus, G; Oszkó, A; Pótári, G; Buzás, N; Dékány, I; Janovák, L;
Photocatalytic performance of silver-modified TiO₂ embedded in poly(ethyl-acrylate-co-methyl metacrylate) matrix
Colloid and Polymer Science, **292**, 207-217 (2014). (IF=2.161)

7 Lectures and poster presentations related to the dissertation

1. János Kiss, Albert Oszkó, Gábor Pótári, András Erdőhelyi:
Role of the nature of the support on the structure of Au-Rh bimetallic nanosystem
13th Joint Vacuum Conference - JVC-13
June 20-24, 2010, Strbské Pleso, Slovakia (oral)
2. Albert Oszkó, Gábor Pótári, István Sarusi, András Erdőhelyi:
XP spectra of Mixed Oxide Supported Rh Catalysts
10th Pannonian International Symposium on Catalysis
29 August - 2 September, 2010, Kraków, Poland (oral)
3. Albert Oszkó, Gábor Pótári, András Erdőhelyi:
Structure of Au-Rh bimetallic system formed on titanate nanowire and nanotube
11th European Vacuum Conference
September 20-24, 2010, Salamanca, Spain (oral)
4. Albert Oszkó, Gábor Pótári, János Kiss, András Erdőhelyi:
Au, Rh and Au-Rh clusters supported on different titania
12th edition of Timisoara's Academic Days
May 26-27, 2011, Timisoara, Romania (oral)
5. Gábor Pótári, László Óvári, Mariann Tóth, Albert Oszkó, János Kiss, András Erdőhelyi:
Structure and Reactivity of Au-Rh Bimetallic Clusters on Titanate Nanostructures and TiO₂(110)
EUROPACAT X Congress
August 27-September 2, 2011, Glasgow, Scotland (poster)
6. Albert Oszkó, Gábor Pótári, Balázs László, András Erdőhelyi, János Kiss:
Adsorption induced morphological changes of Au-Rh nanoparticles on titania and titanate nanostructures
14th Joint Vacuum Conference - JVC-14
June 4-8, 2012, Dubrovnik, Croatia (oral)
7. Gabriella Merza, Balázs László, Albert Oszkó, Gábor Pótári, Kornélia Baán, András Erdőhelyi:
The synthesis of dimethyl carbonate by oxidative carbonylation of methanol on different carbon supported Cu, Ni and Cu-Ni catalysts Carbocat V Conference
June 28-30, 2012, Brixen, Italy (oral)

8. Mariann Tóth, János Kiss, Gábor Pótári, Balázs László, Albert Oszkó, András Erdőhelyi:
Structure and activity of Au-Rh bimetallic clusters supported on titanate nanowire and nanotube
15th International Congress on Catalysis
July 1-6, 2012, Munich, Germany (poster)
9. Albert Oszkó, Mariann Tóth, János Kiss, Gábor Pótári, Balázs László, András Erdőhelyi:
Structure and activity changes of different titania-supported Au-Rh catalysts
11th Pannonian International Symposium on Catalysis
September 3-7, 2012, Obergurgl, Austria (oral)
10. János Kiss, Dániel Madarász, Gábor Pótári, Balázs László, András Sági, László Nagy, Albert Oszkó, Ákos Kukovecz, Zoltán Kónya, András Erdőhelyi:
Structure and stability of clean and Au-Rh containing titanate nanowires and nanotubes
European Conference on Surface Science (CMD-24, ECOSS-29, CMMP-12, ECSCD-11)
September 2-7, 2012, Edinburgh, Scotland (oral)