

Doctoral (Ph.D.) theses

**Surface and structural characterization of CeO₂
supported Rh-Co catalysts**

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1. Introduction and objective

Heterogeneous catalytic reactions have been playing more and more important role in the industry because of the recent heavy demands for raw materials and energy, which make the development of efficient, environmentally friendly, cheap and regenerable catalysts desirable. This task can be solved only with long-term scientific work and modern methods.

Chemical reactions take place over the surface of the catalyst, so the study of the catalytically active layer is uneasy, as the upper atomic layers change faster than the bulk phase. This part of the material possesses special physical-chemical properties, which are influenced by both the bulk phase and the atmosphere around the sample under the experimental circumstances. Catalysis has a strong relationship with nanotechnology, in which the novel properties can be attributed to the high portion of the atoms residing on the surface. In fact, nanoobjects appeared in catalysis already a few decades ago, and today great attempts are being made to create the right structures by design and to tune the properties this way. Without the appropriate examination tools this is an unsolvable problem, too.

Several methods are available to study the morphology of the samples (e.g. SEM, XRD, LEED) or the bonds (e.g. EXAFS) but most of them suit the models systems only, and do not provide us with sufficient information or can damage the surface (SIMS). Among the techniques for surface examination X-ray photoelectron spectroscopy (XPS) excels, it is proper for quantitative analysis and for the determination of the oxidation states of the elements. Concerning the low energy ion scattering spectroscopy (LEIS), its greatest advantage is that it informs us about the elemental composition of the top-most atomic layer.

In general, the catalysts under study are complex systems with support or additives, and they often consist of even nanoparticles. Nanotechnology can make the application of expensive compounds economical, due to the higher efficiency and lower consumption of material. However, researchers try to find substitutes for the noble metals, thus the catalysts made from transition metals have gained attention. Co was proved to be active in several reactions such as the steam reforming of ethanol, the $\text{CO}_2 + \text{H}_2$ and the $\text{CO}_2 + \text{CH}_4$ reactions, or the Fischer-Tropsch synthesis. Each of these processes is important in environmental protection and in the industry, too. In addition, it has been noticed that the catalytic behavior of the transition metals can be further improved by doping with trace amounts of noble metals.

My doctoral work was inspired by the results obtained earlier in our research group relating to the steam reforming of ethanol. My colleagues found that among the Co catalysts, the CeO_2 supported samples had both good ethanol conversion and H_2 selectivity data, but the

samples with Al_2O_3 or SiO_2 support did not meet at least one of these requirements. The activity of the Co/CeO_2 samples increased further when trace amounts of Rh were added. The aim of my three-year-long research was to characterize the structure of Rh-Co/CeO_2 catalysts, especially their surfaces, after simple physical-chemical modifications.

The Rh-Co powder samples with various Rh-Co contents were prepared by impregnation. The primary method to characterize them was XPS, but TEM, XRD and CO adsorption measurements were also carried out to investigate the particle size and crystallinity. By Raman spectroscopy and diffuse reflectance spectroscopy I managed to study the defects and the band gap in CeO_2 . LEIS was useful to reveal the decoration-dissolution effects, and the semiconductor properties were analyzed by photovoltammetry.

The aim of my examinations was to investigate the Rh-Co interaction, and in doing so, the study of the pure support was inevitable, too. I carried out simple experiments over the samples such as oxidation-reduction and heat treatment. The simultaneous effects of oxidizing and reducing reagents were presented during the steam reforming of ethanol.

2. Experimental section

The catalysts were prepared by impregnating the CeO_2 support (Alfa Aesar, $43 \text{ m}^2\text{g}^{-1}$, calcined at 773 K) with the aqueous solution of $\text{Co}(\text{NO}_3)_2$ to yield a nominal metal content of 2 or 10 wt%. The impregnated powders were calcined at 973 K. The Rh containing samples were dried at 397 K after impregnation with RhCl_3 (0.1, 1 or 5 wt% Rh).

XP spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical electron energy analyzer. In our experiments we applied the $\text{Al K}\alpha$ radiation with a power of 210 W (14 kV, 15 mA). The analyzer was operated in the FAT mode with the 'pass energy' set to 30 eV in the case of wide scans and 20 eV for the high resolution spectra. The binding energy scale was corrected by fixing the $\text{Ce 3d u}'''$ peak (Burroughs notation) to 916.6 eV. Sample treatments could be carried out in a high-pressure cell (HPC) connected to the analysis chamber via a gate valve. In this chamber, a bell shaped unit was lowered onto the sample that was treated here in flowing gas at atmospheric pressure. The sample holder in the chamber was heated by electron bombardment from below.

LEIS measurements were carried out within the same instrument. He^+ ions were accelerated by 800 V in a SPECS IQE 12/38 ion source. The ion flux was $200 \text{ nA}\cdot\text{cm}^{-2}$, and to etch the surface Ar^+ ions with 4000 V acceleration were used ($700 \text{ nA}\cdot\text{cm}^{-2}$).

BET surface and pore volume measurements of the catalysts were carried out by a Quantachrome NOVA 3000e instrument using N₂ adsorption at liquid nitrogen temperature. BET (Brunauer, Emmett, Teller) and HJB (Halenda, Joyner, Barrett) methods were applied to determine the specific surface area and the pore volume, respectively.

Temperature programmed reduction experiments were carried out by a BELCAT-A instrument. Before the measurements, the catalysts were treated in O₂ at 673 K for 30 min. Thereafter, the samples were cooled in flowing Ar to room temperature and we let the temperature equilibrate for 15 min. The oxidized sample was flushed with Ar containing 10% H₂, the reactor was heated linearly at a rate of 20 K·min⁻¹ up to 1373 K and the H₂ consumption was detected by a thermal conductivity detector (TCD).

The TEM images were created by a FEI Tecnai G² 20 X-Twin transmission electron microscope with 200 kV operation voltage, ×180000 magnification and 125 pm/pixel resolution.

The XRD study was carried out in a Rigaku Miniflex II powder X-ray diffractometer equipped with a Cu K α radiation source ($\lambda = 0.15418$ nm) by applying a scanning rate of 4°·min⁻¹ in the 2 θ range of 3–80°. The average crystallite size was calculated from the Scherrer equation.

DRIFT spectra were recorded with an Agilent CARY-670 FTS-135 FT-IR spectrometer equipped with an MCT detector heated with liquid N₂ and a diffuse reflectance attachment with BaF₂ windows.

Raman spectra were measured at 532 nm laser excitation (an incident laser power of 10 mW) using a Thermo Scientific DXR Raman spectrometer. Scans were integrated at 4 cm⁻¹ resolution until the desired signal-to-noise ratio of 1000 or better was achieved.

The diffuse reflectance UV-vis spectra of the powdered samples were recorded by an Avantes AvaSpec2048 Fiber Optic Spectrometer equipped with an Avasphere-50 type integrating sphere. The optical bandgap of the prepared materials was estimated by deriving the appropriate Tauc-plots.

Electrochemical measurements were performed in an Autolab PGSTAT302 instrument, in a classical one-compartment, three-electrode electrochemical cell. The various semiconductor nanoparticles were spray coated on glassy carbon electrodes and were used as working electrodes. A large Pt foil counter-electrode and an Ag/AgCl/3 M KCl reference electrode completed the cell setup. The light source was a 300 W Hg-Xe arc lamp (Hamamatsu L8251).

In order to study the surface structure evolved during the reaction at high temperature, the catalysts, oxidized previously at 673 K for 30 min and reduced at 773 K for 1 h, were heated in N₂ atmosphere to 773 K and XP spectra were taken at every 100 K step of temperature increase.

In the stream reforming of ethanol, we oxidized the samples at 673 K and reduced them at 773 K. Ethanol:water mixture in 1:3 ratio was introduced into an evaporator by a HPLC pump (Younglin) at 0.007 mL·min⁻¹ flow rate. The vapour was flushed by N₂ with 60 mL·min⁻¹ onto the sample surface in the HPC of the XPS instrument. The temperature was increased from room temperature to 773 K at a rate of 20 K·min⁻¹.

In the experiments concerning sintering, after oxidation at 673 K for 30 minutes, the samples were reduced in 15 min periods, and in between the temperature was increased by 25-50 K from room temperature up to the full reduction of Rh. After that, the samples were heated at 773 K under 10⁻⁸ mbar pressure for 1 h twice, and then oxidized at 673 K for half an hour, also twice.

3. Summary of new scientific results

1. In the case of CeO₂ supported Co samples, Co²⁺ ions dissolve into the CeO₂ support during reduction at 773 K. In addition to the depletion in Co of the surface atomic layers, which was verified with both XPS and LEIS, this process induced the decrease of the CeO₂ crystallite size that can be enhanced by increasing the Co content (XRD, TEM). This reaction was hindered by the addition of Rh that raises the ratio of metallic Co under the reduction.
2. When CeO₂ supported Co and Rh samples were heated in inert atmosphere after reduction at 773 K, XPS revealed the migration of the support oxygen onto the metals.
 - 2.1. On the samples, that consisted of both Co²⁺ and Co⁰ initially, all the metal oxidized to Co²⁺ and diffused onto the surface up to 573 K. In the temperature range of 573-773 K there was no additional change. This process was independent of the Co loading and the Rh additive.
 - 2.2. The totally reduced Rh oxidized partially and reversibly. In certain periods of the heating different Rh^{δ+}/Rh ratios were calculated that were independent of the Rh loading and the temperature. By the study of Rh+Co/CeO₂ systems it was verified

that the oxidation of Rh was hindered by Co, probably due to the competition for the oxygen species.

- 2.3. In a separate experiment, I proved that the component, which oxidized the metals, originated from the CeO₂. When a strongly reduced CeO₂ surface was heated in vacuum, it oxidized totally, so the oxygen ions in the bulk phase became mobile under the heating and segregated. The oxygen that appeared on the surface can adsorb on the supported metals ('O-spill over').
- 2.4. When an oxidized Rh/CeO₂ sample was heated in vacuum for 1 hour, the reduction of both the Rh and the CeO₂ was detected. With comparison to the metal-free CeO₂, this supports the idea that Rh catalyzes the oxygen loss of the sample surface.
3. In the steam reforming of ethanol it was shown that due to the simultaneous effects of oxidizing and reducing reagents the oxidation state of Co changed towards an equilibrium composition consisting of both Co²⁺ and Co⁰ states. The promoting effect of Rh in the H₂ selectivity is caused by the enhanced Co reduction.
4. According to the literature data, I created a spectrum series concerning the reduction of Rh on CeO₂ support for the first time. The results revealed that depending on the metal loading, the whole Rh content can be reduced between 373 and 423 K. In the transient states definite Rh^{δ+}/Rh ratios are stable, the value of which depends on the temperature.
5. Different particle size changes of CeO₂ supported Rh were detected by XPS and TEM under heat treatment in vacuum, H₂ and O₂ atmospheres.
 - 5.1. I found that even at higher metal loading (5%) well-dispersed Rh particles could be found over the CeO₂ surface. During heat treatment, a larger loss of the surface was detected in the case of 1% Rh/CeO₂ sample due to the different particle size distribution and metal density on the surface.
 - 5.2. After oxidation during the pretreatments I noticed that the Rh particle size increase is hindered during heating in O₂ atmosphere, however, in H₂ it was remarkable. When the heat treatment was carried out in vacuum, sintering happened but this effect was not significant in this case.
 - 5.3. On the samples that contained also Co, the sintering was not observed in vacuum, but in H₂ it took place.
 - 5.4. When the sintered samples were oxidized, Rh oxides were produced and the particle sizes decreased supposedly. Based on that Rh-O-Ce bond formation was evidenced

in the literature, we suppose that the formation and the cleavage of them cause the different particle size changes in the different atmospheres: in vacuum and more easily in H₂ they break and sintering can happen. In oxygen, Rh-O-Ce bonds are formed inhibiting the Rh particle size increase, and the larger particles disrupt.

- 5.5. During heat treatment in vacuum, a negative shift of the Rh 3d peak position was observed compared to the Rh metal, which refers to the alteration in the metal-support electronic interaction and to the electron transfer from the support to the metal.

6. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10040544

Publications related to the topic of the dissertation:

1. **E. Varga**, P. Pusztai, A. Oszkó, K. Baán, A. Erdőhelyi, Z. Kónya, J. Kiss:
Stability and temperature induced agglomeration of Rh nanoparticles supported by CeO₂
Langmuir 32 (2016) 2761–2770. **IF₂₀₁₅: 4.457**
2. **E. Varga**, P. Pusztai, L. Óvári, A. Oszkó, A. Erdőhelyi, C. Papp, H.-P Steinrück, Z. Kónya, J. Kiss:
Probing the interaction of Rh, Co and bimetallic Rh–Co nanoparticles with the CeO₂ support: catalytic materials for alternative energy generation
Physical Chemistry Chemical Physics, 17 (2015) 27154-27166. **IF₂₀₁₅: 4.493**
3. **E. Varga**, Zs. Ferencz, A. Oszkó, A. Erdőhelyi, J. Kiss:
Oxidation states of active catalytic centers in ethanol steam reforming reaction on ceria based Rh promoted Co catalysts: an XPS study
Journal of Molecular Catalysis A: Chemical 397 (2015) 127–133. **IF₂₀₁₅: 3.615**

ΣIF= 12.565

Other publications:

4. L. Balázs, K. Baán, E. Varga, A. Oszkó, A. Erdőhelyi, Z. Kónya, J. Kiss:
Photo-induced reactions in the CO₂-methane system on titanate nanotubes modified with Au and Rh nanoparticles: Production of hydrogen
Applied Catalysis B: Environmental elfogadott **IF₂₀₁₅: 8,328**
5. G. Varga, Sz. Ziegenheim, Sz. Murath, Z. Csendes, A. Kukovecz, Z. Konya, S. Carlson, L. Korecz, **E. Varga**, P. Pusztai, P. Sipos, I. Palinko:
Cu(II)-amino acid-CaAl-layered double hydroxide complexes, recyclable, efficient catalysts in various oxidative transformations
Journal of Molecular Catalysis A: Chemical 423 (2016) 49-60. **IF₂₀₁₅: 3.615**
6. É. Horváth, K. Baán, **E. Varga**, A. Oszkó, Á. Vágó, M. Törő, A. Erdőhelyi:
Dry reforming of CH₄ on Co/Al₂O₃ catalysts reduced at different temperatures
Catalysis Today 2016 doi:10.1016/j.cattod.2016.04.007 **IF₂₀₁₅: 3.893**
7. M. Tóth, **E. Varga**, A. Oszkó, K. Baán, J. Kiss, A. Erdőhelyi:
Partial oxidation of ethanol on supported Rh catalysts: Effect of the oxide support
Journal of Molecular Catalysis A: Chemical 411 (2016) 377-387. **IF₂₀₁₅: 3.615**
8. G. Merza, B. László, A. Oszkó, G. Pótári, **E. Varga**, A. Erdőhelyi:
The synthesis of dimethyl carbonate by the oxycarbonylation of methanol over Cu supported on carbon Norit
Catalysis Letters 145 (2015) 881–892. **IF₂₀₁₅: 2.307**
9. Gy. Halasi, T. Bánsági, **E. Varga**, F. Solymosi:
Photocatalytic decomposition of formic acid on Mo₂C-containing catalyst
Catalysis Letters 145 (2015) 875–880. **IF₂₀₁₅: 2.307**
10. **E. Varga**, M. Varga:
Development and validation of an LC-MS/MS method for the analysis of L-DOPA in oat
Acta Biologica Szegediensis 58 (2014) 133-137. **IF₂₀₁₅: 0**
11. G. P. Szekeres, K. Nemeth, A. Kinka, M. Magyar, B. Reti, **E. Varga**, Zs. Szegletes, A. Erdőhelyi, L. Nagy, K. Hernadi:
Segmental nitrogen doping and carboxyl functionalization of multi-walled carbon nanotubes
Physica Status Solidi B 252 (2015) 2472-2478. **IF₂₀₁₅: 1.489**

12. T. Csizmadia, T. Smausz, Cs. Tápai, J. Kopniczky, X. Wang, M. Ehrhardt, P. Lorenz, K. Zimmer, L. Orosz, **E. Varga**, A. Oszkó, B. Hopp:
Comparison of the production of nanostructures on bulk metal samples by picosecond laser ablation at two wavelengths for the fabrication of low-reflective surfaces
 Journal of Laser Micro Nanoengineering 10 (2015) 110-118. **IF₂₀₁₅: 1.008**

13. P. Pusztai, R. Puskás, **E. Varga**, A. Erdőhelyi, Á. Kukovecz, Z. Kónya, J. Kiss:
Influence of gold additives on the stability and phase transformation of titanate nanostructures
 Physical Chemistry Chemical Physics 16 (2014) 26786–26797. **IF₂₀₁₅: 4.493**

14. É. A. Enyedy, O. Dömötör, **E. Varga**, T. Kiss, R. Trondl, C. G. Hartinger, B. B. Keppler:
Comparative solution equilibrium studies of anticancer gallium(III) complexes of 8-hydroxyquinoline and hydroxy(thio)-pyrone ligands
 Journal of Inorganic Biochemistry 117 (2012) 189–197. **IF₂₀₁₂: 3.197**

15. E. Csapó, A. Oszkó, **E. Varga**, Á. Juhász, N. Buzás, L. Körösi, A. Majzik, I. Dékány:
Synthesis and characterization of Ag/Au alloy and core(Ag)–shell(Au) nanoparticles
 Colloids and Surfaces A: Physicochemical and Engineering Aspects 415 (2012) 281–287. **IF₂₀₁₂: 2.108**

ΣΣIF= 46.618

Conference presentations related to the topic of the dissertation:

1. **E. Varga**, P. Pusztai, A. Oszkó, J. Kiss, A. Erdőhelyi, Z. Kónya:
Temperature induced structural changes of Co-Rh/ceria catalysts
 31st European Conference on Surface Science
 30 August-4 September 2015, Barcelona, Spain poster presentation

2. **E. Varga**, K. Baán, A. Erdőhelyi, D. Madarász, Á. Kukovecz, A. Oszkó, Z. Kónya, J. Kiss:
Interaction of rhodium with ceria supported cobalt nanoclusters
 The Seventh Edition of the Symposium with International Participation- New Trends and Strategies in the Chemistry of Advanced Materials with Relevance in Biological Systems, Technique and Environmental Protection
 5-6 June 2014, Timisoara, Romania oral presentation

3. **E. Varga**, A. Erdőhelyi, A. Oszkó, J. Kiss, Zs. Ferencz:
XPS characterization of CeO₂ and Al₂O₃ supported Co-Rh catalysts during the steam reforming reaction of ethanol
 12th Pannonian Symposium on Catalysis
 16-20 September 2014, Třešt, Czech Republic oral presentation

4. **E. Varga**, K. Baán, A. Erdőhelyi, D. Madarász, Á. Kukovecz, A. Oszkó, Z. Kónya, J. Kiss:
Interaction of rhodium with cobalt nanoclusters on CeO₂
 15th Joint Vacuum Conference
 15-20 June 2014, Vienna, Austria poster presentation

Other conference presentations:

5. E. Horváth, K. Baán, **E. Varga**, A. Oszkó, B. László, A. Erdőhelyi:
Dry reforming of CH₄ on different supported Co catalysts
 11th Natural Gas Conversion Symposium
 5-9 June 2016, Tromsø, Norway oral presentation

6. J. Kiss, B. Buchholcz, **E. Varga**, T. Varga, Z. Kónya:
Structure and stability of boron doped titanate nanotubes and nanowires
 16th Joint Vacuum Conference/14th European Vacuum Conference
 6-10 June 2016, Portoroz, Slovenia oral presentation

7. G. P. Szekeres, K. Németh, A. Kinka, M. Magyar, B. Réti, **E. Varga**, Zs. Szegletes, A. Erdőhelyi, L. Nagy, K. Hernádi:
Controlled nitrogen doping and carboxyl functionalization of MWCNTs
 28th International Winterschool on Electronic Properties of Novel Materials
 7-14 March 2015, Kirchberg in Tirol, Austria poster presentation
8. J. Kiss, **E. Varga**, A. Erdőhelyi, A. Oszkó, K. Baán, L. Óvári, C. Papp, H.-P. Steinrück, Z. Kónya:
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 Rideal Conference
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9. Zs. Ferencz, K. Baán, **E. Varga**, A. Oszkó, A. Erdőhelyi:
Reforming of ethanol on Co/Al₂O₃ catalyst reduced at different temperatures
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 12-14 March Sevilla, Spain oral presentation
10. P. Pusztai, L. Nagy, Á. Kukovecz, **E. Varga**, A. Erdőhelyi, J. Kiss, Z. Kónya:
Formation and characterization of gold nanoparticles on titanate nanotubes and nanowires
 15th Joint Vacuum Conference
 15-20 June 2014, Vienna, Austria oral presentation
11. **E. Varga**, M. Varga, R. Mihály, A. Palágyi:
Determination of L-DOPA in different oat varieties by LC-MS/MS
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 4-6 September 2013, Siófok, Hungary poster presentation
12. O. Dömötör, **E. Varga**, K. Bali, C. G. Hartinger, B. B. Keppler, T. Kiss, É. A. Enyedy:
Solution studies on antitumor gallium(III) complexes and their interactions with human serum proteins
 International Symposium on Metal Complexes 2012
 18-22 June 2012, Lisbon, Portugal poster presentation