

Boriskov Institute of Catalysis  
Fritz Haber Institute of the Max Planck Society



BORESKOV INSTITUTE  
OF CATALYSIS

5<sup>th</sup> Russian-German Seminar  
“Bridging the Gap  
between Model and Real Catalysis”



MAX-PLANCK-GESELLSCHAFT

# Synchrotron Radiation in Catalysis



June 23-26, 2019  
Novosibirsk, Russia

## ABSTRACTS

Novosibirsk-2019

**Boreskov Institute of Catalysis  
Fritz Haber Institute of the Max Planck Society**

**5<sup>th</sup> Russian-German Seminar  
“Bridging the Gap  
between Model and Real Catalysis”  
Synchrotron Radiation in Catalysis**

**June 23-26, 2019  
Novosibirsk, Russia**

# **Abstracts**

**Novosibirsk, 2019**

**УДК 544.47+544.6**  
**ББК 24.54**  
**B-86**

**B-86 Bridging the Gap between Model and Real Catalysis. Synchrotron Radiation in Catalysis. 5<sup>th</sup> Russian-German Seminar / June 23-26, 2019, Novosibirsk, Russia / [Electronic resource] : Abstracts / Boreskov Institute of Catalysis; eds.: Prof. Valerii I. Bukhtiyarov, Dr. Marina V. Bukhtiyarova – Novosibirsk : BIC, 2019.**  
– [http://catalysis.ru/resources/institute/Publishing/Report/2019/ABSTRACTS\\_RGS\\_on\\_Catalysis2019.pdf](http://catalysis.ru/resources/institute/Publishing/Report/2019/ABSTRACTS_RGS_on_Catalysis2019.pdf)  
– ISBN 978-5-906376-23-7

*В надзаг.:* Boreskov Institute of Catalysis  
Fritz Haber Institute of the Max Planck Society

The main topics are:

- In situ and operando studies of model and real catalysts.
- Advanced synchrotron methods in catalysis.
- Electrocatalysis.

**УДК 544.47+544.6**  
**ББК 24.54**

## Organised by

Boreskov Institute of Catalysis, Novosibirsk, Russia  
&  
Fritz Haber Institute of the Max Planck Society, Berlin, Germany



BORESKOV INSTITUTE  
OF CATALYSIS



MAX PLANCK GESELLSCHAFT

## Scientific Committee

<b>Prof. Dr. Valerii I. Bukhtiyarov</b>	Boreskov Institute of Catalysis, Novosibirsk, Russia
<b>Prof. Dr. Robert Schlögl</b>	Fritz Haber Institute of the Max Planck Society, Max Planck Institute for Chemical Energy Conversion, Berlin, Germany
<b>Prof. Dr. Alexander Yu. Stakheev</b>	Zelinsky Institute of Organic Chemistry, RAS, Moscow, Russia
<b>Prof. Dr. Ekaterina.S. Lokteva</b>	Lomonosov Moscow State University, Moscow, Russia

## Organizing Committee

<b>Prof. Dr. Valerii I. Bukhtiyarov</b>	Boreskov Institute of Catalysis, Novosibirsk, Russia
<b>Prof. Dr. Axel Knop-Gericke</b>	Fritz Haber Institute of the Max Planck Society, Berlin, Germany
<b>Dr. Marina V. Bukhtiyarova</b>	Boreskov Institute of Catalysis, Novosibirsk, Russia
<b>Dr. Vasily V. Kaichev</b>	Boreskov Institute of Catalysis, Novosibirsk, Russia

## Secretariat

<b>Marina S. Suvorova</b>	Boreskov Institute of Catalysis, Novosibirsk, Russia
<b>Dorothea Damm</b>	Fritz Haber Institute of the Max Planck Society, Berlin, Germany

The scientific program of seminar includes six plenary lectures (40 min) and presentations (20 min).

The main topics are:

- In situ and operando studies of model and real catalysts.
- Advanced synchrotron methods in catalysis.
- Electrocatalysis.



## **Plenary Lectures**

**PL-1 ÷ PL6**



## PL-1

# The Electronic Structure of Solid/Liquid Interfaces Relevant for Water Oxidation and Carbondioxide Reduction

Knop-Gericke A.

1 – MPI for Chemical Energy Conversion, Mülheim, Germany

2 – Fritz-Haber-Institute of the MPG, Berlin, Germany

*knop@fhi-berlin.mpg.de*

In this lecture I will give an overview on the application of ambient pressure X-ray photoelectron spectroscopy on the investigation of electrochemical reactions like the oxygen evolution reaction (OER) and the CO<sub>2</sub> reduction (CO<sub>2</sub>RR) [1-3]. The development of different in situ cells has revealed new insights into the reaction mechanism of the OER and the synthesis valuable C<sub>2</sub> compounds by CO<sub>2</sub>RR.

The electrochemically prepared copper-redox electro-cathodes yield higher activity for the production of hydrocarbons at lower oxidation state. By combining advanced X-ray spectroscopy and in situ microreactors, it was possible to unambiguously reveal the variation in the complex electronic structure that the catalysts undergo at different stages [1].

Iridium oxide-based catalysts are uniquely active and stable in the oxygen evolution reaction. Theoretical work attributes their activity to oxyl or  $\mu_1$ -O species. Verifying this intermediate experimentally is challenging. These challenges were overcome by combining theory with potentiodynamic X-ray absorption spectroscopy [2].

**Acknowledgement.** This work was supported by BMBF (SIMPLANT, GEP).

### References:

- [1] J. J. Velasco-Velez, T. E. Jones et al. ACS Sustainable Chemistry&Engineering 7, 1485-1492, 2019.
- [2] L. J. Frevel, R. Mom, J. J. Velasco-Velez et al. Journal of Physical Chemistry C 123, 9146-9152, 2019.
- [3] J. J. Velasco-Velez, T. E. Jones, V. Streibel, M. Hävecker et al. Surface Science 681,1-8,2019.



## Structural Diagnostics of Catalysts Using X-Ray Synchrotron Radiation: Current Possibilities and Future Prospects

Zubavichus Y.V.

*Boreshkov Institute of Catalysis, Novosibirsk, Russia*

*yvz@catalysis.ru*

In the present contribution, some recent results by the author in the field of structural studies of catalysts are surveyed. Most experimental data were obtained at several beamlines of the Kurchatov Synchrotron Radiation Source (NRC “Kurchatov Institute”, Moscow). The techniques discussed include single-crystal and powder X-ray diffraction, X-ray Absorption Spectroscopy XANES/EXAFS, Small-Angle X-ray Scattering, etc.

Some examples concern cage polynuclear metal-containing organosiloxanates manifesting a pronounced catalytic activity in homogeneous oxidation, which is demonstrated by X-ray crystallographic identification of products of spontaneous and completely unexpected mild oxidation of ligands or solvents under synthesis conditions, including conversions of alcohol into carboxylate, THF into butyrolactone, phosphine into phosphine oxide, aromatic methyl of neocuproine into geminal diol.

Another series of examples include structural monitoring of formation of catalytically active bimetallic nanoparticles from mixed-acetate molecular precursors (Pd-Zn, Pd-Ni, Pd-Eu, Pd-In, Pd-Pt, etc.). X-ray diffraction and XAFS implemented *in situ* make it possible to identify the sequence of distinct stages of the overall process initiated at different temperatures, such as chemical reduction of palladium, onset of reduction of the second metal, disordered solid solution emergence, intermetallic ordering, thermally activated growth of nanoparticles, etc. This knowledge enables fine control over the formation of nanoparticles to tailor their catalytic properties.

As the final part of the talk, a brief introduction into new capabilities for the advanced diagnostics of catalysts imposed by the SKIF (Siberian Circular Photon Source), which is a project of a 4<sup>th</sup>-generation synchrotron centre near Novosibirsk being jointly developed by the Boreshkov Institute of Catalysis and Budker Institute of Nuclear Physics, will be given.

**Acknowledgement.** This work was supported by Ministry of Science and Higher Education of the Russian Federation (project AAAA-A19-119020890025-3).

## Electrocatalysis at the Molecular Level: from Electrochemical Methods to In Situ Spectroscopies

Savinova E.R.

UMR 7515 CNRS - University of Strasbourg, Strasbourg, France

*elena.savinova@unistra.fr*

One of the greatest global challenges facing the human society is a gradual transition from the fossil fuel- to the renewable energy-based economy. The intermittent character of renewable energy sources motivates the development of technologies for production of solar fuels, such as hydrogen, and their efficient back conversion into electricity on demand. Electrocatalysis plays pivotal role in the transition of our society to the renewable energy-based economy. It should be stressed that the development of efficient energy conversion systems not only requires potent, durable and cost-effective materials, but also asks for precise engineering of electrochemical interfaces where molecular, ionic and electronic flows merge. Future progress in the field thus requires understanding of electrocatalytic processes and materials at the molecular level.

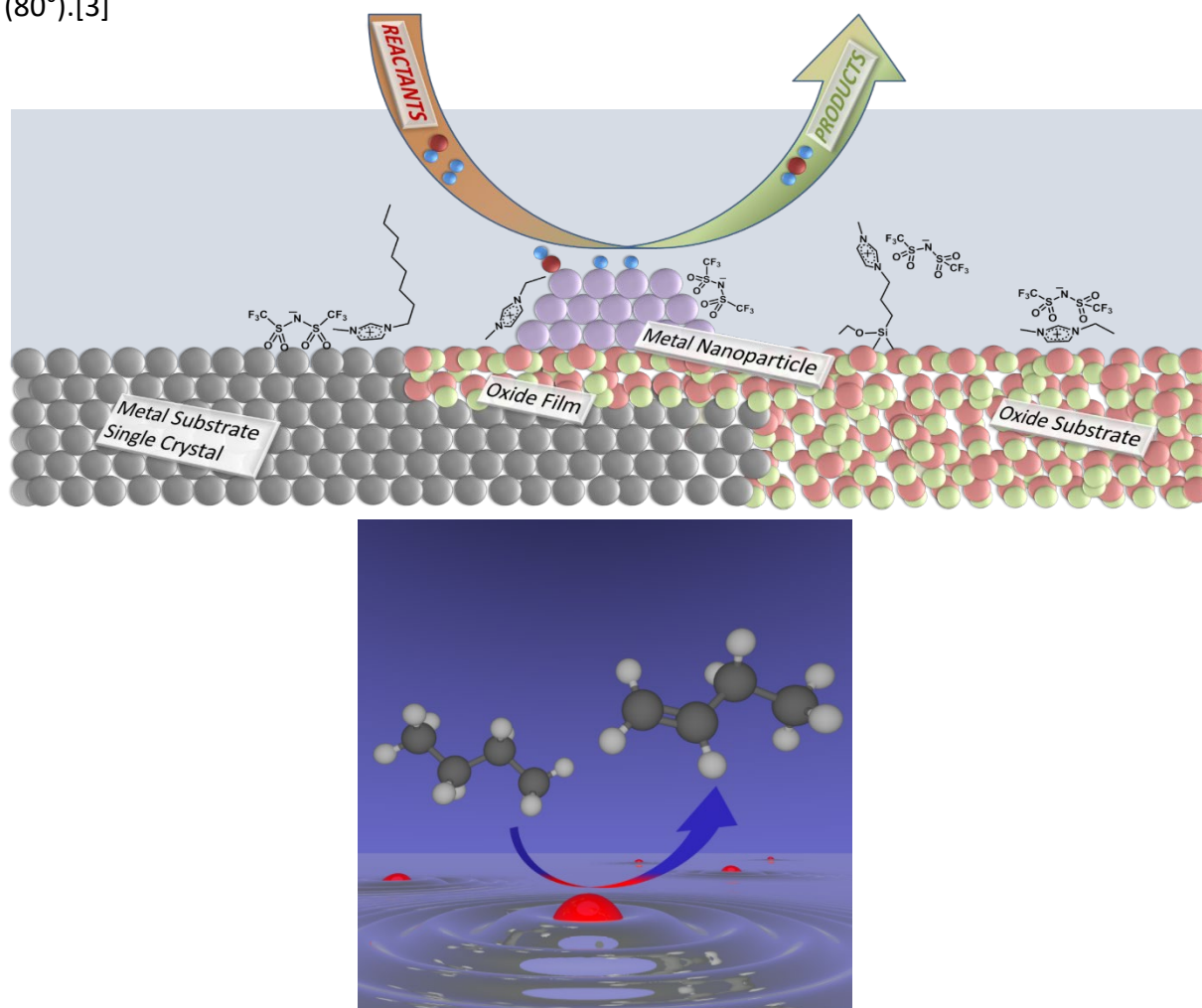
Various approaches can be utilized nowadays in order to obtain either direct or indirect information regarding the mechanisms of electrocatalytic reactions and the nature of active intermediates, among them electrochemical methods, *operando* spectroscopies, *ab initio* calculations and kinetic modeling. In this presentation we will illustrate these approaches by considering several case studies related to the electrochemical energy conversion systems.

## Surface Science of Low Vapor Pressure Liquids

Steinrück H.-P.

*Physical Chemistry, University Erlangen-Nürnberg, Erlangen, Germany*

Low-vapor-pressure liquids can be investigated using the methods surface science. In particular, angle-resolved XPS provides access to the liquid/gas(vacuum) and liquid/solid interfaces. It even allows for *in situ* studies of chemical reactions in the liquid. We report on recent investigations of ionic liquids [1] and of novel supported liquid metal catalysts.[2] The experiments were performed with our near-ambient pressure XPS lab setup, and with a newly developed two-analyzer lab-based XPS system that allows for simultaneous measurements of low-viscosity liquids at normal ( $0^\circ$ ) and grazing emission ( $80^\circ$ ).[3]



### References:

- [1] F. Maier, I. Niedermaier, H.-P. Steinrück, *J. Chem. Phys.* 146 (2017) 170901 1-15.
- [2] N. Taccardi, M. Grabau, ...C. Papp, H.-P. Steinrück, P. Wasserscheid, *Nat. Chem.* 9 (2017) 862.
- [3] I. Niedermaier, C. Kolbeck, H.-P. Steinrück, F. Maier, *Rev. Sci. Instrum.* 87 (2016) 045105.

## Time-Resolved and Operando Photoemission Studies on Metal Oxide Photoelectrodes

Van de Krol R., Friedrich D., Eichberger R., Favaro M., Starr D.E.

*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Solar Fuels, Berlin, Germany*

The photo-driven conversion of water and CO<sub>2</sub> into chemical fuels represents an exciting new pathway for the combined conversion and storage of solar energy in the form of chemical bonds. Since hydrogen is a key ingredient of *all* chemical fuels, efficient and scalable solar-powered water splitting is an important building block for these efforts. Our group explores direct photoelectrochemical (PEC) water splitting at functionalized semiconductor surfaces. This allows the use of solar heat to enhance the electrochemical reaction kinetics and thereby offers an important advantage over photovoltaics-powered electrolysis [1].

One of the main challenges in solar-driven water splitting is to find stable and efficient light absorbers with a bandgap of 1.7-1.9 eV. When used in combination with a suitable small-bandgap bottom absorber in a dual absorber tandem device, solar-to-hydrogen efficiencies of more than 20% are theoretically possible. One potential candidate is Cu<sub>2</sub>O, a p-type semiconductor with a bandgap of about 2.0 eV. Recent work by Grätzel et al. have shown impressive performance [2], but the photovoltage is still well below what is theoretically possible. We used femtosecond time-resolved two-photon photoemission spectroscopy (tr-2PPE) to follow the energetics and dynamics of photoexcited electrons at the Cu<sub>2</sub>O(100) surface [3]. We find that photoexcited electrons are rapidly trapped in bulk defect states. In fact, no electrons are able to reach the surface at energies that correspond to the conduction band level. This shows that bulk trapping limits the accessible photovoltage of the material. Whereas photoexcited electrons show relatively long lifetimes (ns) at reconstructed Cu<sub>2</sub>O(100) surfaces, a Pt adlayer enables quick extraction of these electrons (Fig. 1). This makes them available for subsequent photochemical reaction steps, but it also reduces the

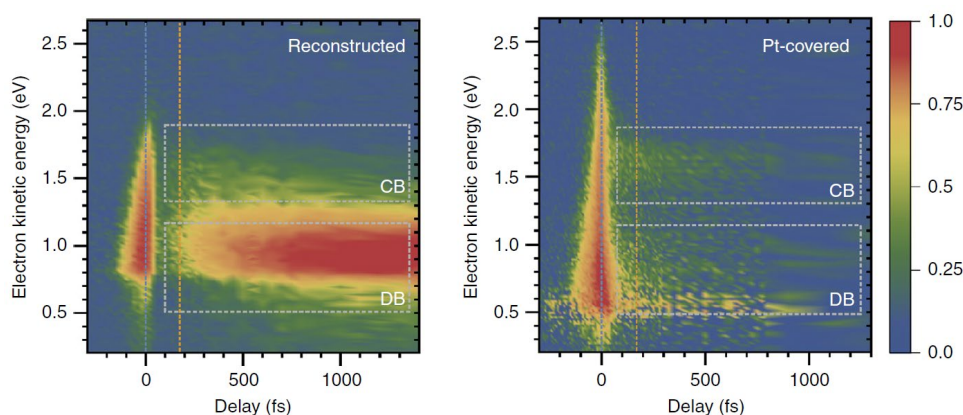


Figure 1. Time-resolved 2PPE spectra of reconstructed and Pt-covered Cu<sub>2</sub>O(100) [3].

## PL-5

accessible photovoltage even further. These findings show that accurate control over both bulk and surface defects is crucial in order to maximize the photovoltage of Cu<sub>2</sub>O photocathodes.

The second part of the talk will be devoted to recent results on bismuth vanadate photoelectrodes. BiVO<sub>4</sub> is a more “defect-tolerant” material than Cu<sub>2</sub>O and has become one of the most-studied photoanode materials for PEC water splitting, despite its larger bandgap (2.4 eV). One of the main challenges is the formation of polarons, which slows down charge transport and leads to photovoltage losses. We previously provided direct evidence for the formation of hole polarons using time-resolved THz spectroscopy [4]. More recent resonant photoemission studies on BiVO<sub>4</sub>(010) crystals showed that Mo doping introduces reduced vanadium species that form intraband gap states which are likely associated with *electron* polaron formation [5]. Of particular interest is the electronic structure of the solid-liquid interface of BiVO<sub>4</sub> photoanodes. Using the “dip-and-pull” method in combination with *in situ* ambient pressure tender X-ray photoelectron spectroscopy at the Advanced Light Source in Berkeley, we previously showed that BiPO<sub>4</sub> is formed under illumination in a phosphate-containing electrolyte [6]. We are expanding these efforts and recently started commissioning a new endstation for Spectroscopy Analysis with Tender X-rays (SpAnTeX) with dip-and-pull capabilities at the BESSY II synchrotron in Berlin. Initial results reveal that BiVO<sub>4</sub> photoanodes in borate-based electrolytes show very different chemical behavior from the above-mentioned phosphate-based electrolytes. Specifically, no chemical interaction between the borate electrolyte and the BiVO<sub>4</sub> is observed. The implications will be discussed and the capabilities of the new SpAnTeX endstation, which is part of the recently established Berlin Joint Lab for Electrochemical Interfaces (BEIChem) between Helmholtz-Zentrum Berlin and the Fritz-Haber-Institute, will be outlined.

**Acknowledgement.** This work was supported by the German Federal Ministry of Education and Research (project “Grundlagen elektrochemischer Phasengrenzen”, #13XP5023C) and the Helmholtz Association through the Excellence Network UniSysCat (ExNet-0024-1).

### References:

- [1] R. van de Krol, B.A. Parkinson, MRS Energy Sustain. 4 (2017) E13.
- [2] L. Pan, J.H. Kim, M.T. Mayer, M.K. Son, A. Ummadisingu, J.S. Lee, A. Hagfeldt, M. Grätzel, Nat. Catal. 1 (2018) 412.
- [3] M. Borgwardt, S.T. Omelchenko, M. Favaro, P. Plate, C. Höhn, D. Abou-Ras, K. Schwarzburg, R. van de Krol, H.A. Atwater, N.S. Lewis, R. Eichberger, D. Friedrich, Nat. Commun. 10 (2019) 2106.
- [4] M. Ziwrtsch, S. Müller, H. Hempel, T. Unold, F.F. Abdi, R. van de Krol, D. Friedrich, R. Eichberger, ACS Energy Lett. 1 (2016) 888.
- [5] M. Favaro, R. Uecker, S. Nappini, I. Piš, E. Magnano, H. Bluhm, R. van de Krol, D.E. Starr, J. Phys. Chem. C 123 (2019) 8347.
- [6] M. Favaro, F.F. Abdi, M. Lamers, E.J. Crumlin, Z. Liu, R. van de Krol, D.E. Starr, J. Phys. Chem. B 122 (2018) 801.

## Microscopic Insights on Properties of Catalysts Using Synchrotron-Based Methods

Kiskinova M.

1 – Elettra-Sinctortrone Trieste, Area Science Park, Trieste-Basovizza, Italy  
maya.kiskinova@elettra.eu

Judging from the number of publications, heterogeneous catalysis is among the most extensively studied functional systems since it is a keystone of chemical industry, fuel and energy production, conversion and storage and also crucial part of the devices for environmental protection. The complexity of catalytic systems is multilevel and needs guided fabrication to attain desired functionality based on the profound knowledge about the evolution in the properties occurring under operation due to modifications or degradation of the catalysts and all other essential building blocks as catalyst supports, electrodes, electrolytes. In this respect the complementary capabilities of synchrotron-based microscopy methods in terms of imaging, spectroscopy, spatial resolution and variable probing depths have opened unique opportunities to explore the structure and chemical composition of morphologically complex catalyst systems at relevant length and time scales and correlate them to the fabrication or operating conditions [1,2].

The topics that will be addressed and discussed in the talk are the events occurring in various types of catalyst systems, uncovered by monitoring the evolution in lateral inhomogeneity in the composition and chemical state at sub-micrometer length scales. The talk will include selected results obtained with scanning X-ray microscopes illustrating (i) compositional complexity of metal catalysts developed under oxidation conditions and correlation of the spatial variations in the chemical composition to the surface morphology [3]; (ii) the effect of growth conditions and aging on the chemical state and space distribution of hybrid electrocatalysts [4, 5]; (iii) monitoring in-situ the lateral evolution of the chemical state and local potential at the electrode/electrolyte interface in solid oxide fuel cells [6].

Ongoing efforts and recent achievements in developing in-operando microscopy experimental set-ups will be outlined and discussed [7].

### References:

- [1] S. Günther et al, Prog. Surf. Sci. 70 (2002) 187 and references therein.
- [2] B. Kaulich et al, J. Phys. Condensed Matter 23 (2011) and references therein.
- [3] M. Amati et al, Surf. Sci. 652 (2016) 20 and references therein.
- [4] B. Bozzini et al, *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering (2015)*  
doi: [10.1016/B978-0-12-409547-2.11452-0](https://doi.org/10.1016/B978-0-12-409547-2.11452-0) and references therein.
- [5] G. Kourousias et al, Nano Res 9 (2016) 2046; Appl. Nanoscience 8(2018) 627.
- [6] B. Bozzini et al, Scientific Reports 3, (2013) 2848; Topics of Catalysis 61 (2018) 2185.
- [7] A. Kolmakov et al, Topics in Catalysis 59 (2016) 448; Microsc. Microanal. 24 (2018) 64 and references therein.



## **Oral Presentations**

**OP-1 ÷ OP-23**





## High Energy X-Ray Synchrotron In Situ and Operando Diagnostics of Heterogeneous Catalysts

Shmakov A.N., Vinokurov Z.S., Yakushkin S.S., Nesterov N.S., Martyanov O.N.  
*Boreskov Institute of Catalysis, Novosibirsk, Russia*  
*shurka@catalysis.ru*

Conventional X-ray structure analysis of functional materials with laboratory diffractometers usually exploits radiation of different metallic anodes which are bombarded with electrons and emit photons of corresponding characteristic energies, for example,  $\text{CuK}\alpha=8.048$  keV ( $\lambda=0.15406$  nm) or  $\text{MoK}\alpha=17.479$  keV ( $\lambda=0.07093$  nm). The highest photon energy commonly used for X-ray diffraction (XRD) experiments is  $\text{AgK}\alpha=22.165$  keV ( $\lambda=0.055936$  nm). However a great number of researches dealing with materials under severe conditions of high temperature and pressure demand much higher photon energy up to 100÷150 keV. The photon beams of high energy and high flux are provided by modern sources of synchrotron radiation.

High energy synchrotron XRD has definite advantage against low and moderate energy experiments. First, the radiation of higher energy is weakly absorbed and can be used to study materials which are confined in special cell with rather thick walls, such as diamond anvil cell for high pressure experiments or autoclave for hydrothermal synthesis. Second, the diffraction angles become smaller with energy rises and necessary information about the structure of material is contained in a limited diffraction angle range. Third, the limited diffraction angle range at high photon energy covers wide range of scattering vectors which can be used for Pair Distribution Function (PDF) analysis. The latter is very suitable for study of structure and structure transformations of specific functional materials with imperfect structure such as heterogeneous catalysts.

The report describes high energy experiments which were executed at VEPP-4M storage ring beamline at Siberian Synchrotron and Terahertz Radiation Center, Novosibirsk, as well as experiments conducted at other facilities both at normal conditions and In Situ and Operando modes.

**Acknowledgement.** This work was supported by Ministry of Science and Higher Education of the Russian Federation (project AAAA-A19-119020890025-3).

### References:

[1] M.A.Newton. Operando catalysis using synchrotron methods, *Catalysis, Structure & Reactivity*, 3:1-2, 2-4, (2017). DOI: 10.1080/2055074X.2017.1281605.

## The Study of Au/Ni Bimetallic Nanoparticles Using a Combination of XAFS, XRD and SAXS/ASAXS Synchrotron Techniques

Belyakova O.A.<sup>1</sup>, Zubavichus Ya.V.<sup>1</sup>, Vasil'kov A.Y.<sup>2</sup>, Naumkin A.V.<sup>2</sup>

*1 – Boreskov Institute of Catalysis, Novosibirsk, Russia*

*2 – A.N.Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia  
olbelyak@gmail.com*

Bimetallic Au/Ni nanoparticles are characterised by a strong size effect and synergism of the catalytic activity towards the allylbenzene isomerization [1]. The Au/Ni nanoparticles prepared by the metal-vapour synthesis (MVS) method as metal-rich blacks and composites supported on various supports were studied via XAFS, XRD and SAXS/ASAXS techniques.

According to the Au L<sub>3</sub>-edge XAFS data the local structural environment of Au atoms in Au/Ni nanoparticles is close to that in the bulk Au. The Au-Au distance (2.78 Å) in Au/Ni nanoparticles is shorter and coordination number is smaller than in bulk Au due to the small particle size. The Au-Ni interaction at 2.74 Å was also observed for Au atoms. According to the Ni K-edge XAFS data the local environment of Ni atoms in Au/Ni nanoparticles is close to that in the nickel oxide NiO.

The XRD data indicate the presence of 1.5-2 nm bulk Au nanoparticles in the bimetallic Au/Ni nanocomposites, whereas nickel oxide phase is completely amorphous. The SAXS signal is dominated by Au and thus it provides a straightforward estimate of gold nanoparticle size that agrees well with the XRD data. The anomalous SAXS technique near the Ni K-edge was used to distinguish the contribution of Ni atoms in Au/Ni nanocomposites. It reveals a wide size distribution of Ni aggregates in the range of 5-50 nm with a maximum at 20 nm.

The combination of XAFS, XRD and SAXS/ASAXS techniques allows one to make a conclusion on Au@NiO core-shell model structure of the bimetallic Au/Ni nanoparticles.

The results on MVS-synthesised Au/Ni nanoparticles were compared with transformations of bimetallic cluster compound [Au<sub>6</sub>Ni<sub>32</sub>(CO)<sub>44</sub>]<sup>6-</sup> in acetonitrile solution giving rise to Au/Ni bimetallic nanoparticles as monitored by in situ EXAFS [2].

**Acknowledgement.** This work was supported by Ministry of Science and Higher Education of the Russian Federation (project AAAA-A19-119020890025-3).

### References:

- [1] A.Y. Vasil'kov, S.A. Nikolaev, V.V. Smirnov, A.V. Naumkin, I.O. Volkov, V.L. Podshibikhin, *Mend Commun* 17 (2007) 268.
- [2] O. A. Belyakova, Y. Kubozono, S. Kashino, Yu. L. Slovokhotov, *Phys. Scr.* T115 (2005) 705.

## On the Mechanism of CO Oxidation on Gold Nanocluster: Ligand and Doping Effects

Pichugina D.A., Nikitina N.A., Kuz'menko N.E.  
*M.V. Lomonosov Moscow State University, Moscow, Russia*  
*nnikitina1719@gmail.com*

The development of a catalyst of low temperature CO oxidation is an important task [1]. Traditional heterogeneous catalysts of CO oxidation contain noble metals nanoparticles, e.g. gold, platinum. The development of active catalysts based on small size-selected nanoclusters with smaller amounts of noble metals is a modern trend. This could be achieved by protection of metal particles by organic ligands or doping of the metal particle by less expensive metals. Therefore, the aim of this work is to predict the ligand and doping effect on the catalytic properties of gold and platinum clusters in CO oxidation using DFT calculation.

Here Pt<sub>13</sub>, Au<sub>13</sub>, Pt<sub>12</sub>X, and Au<sub>12</sub>X (X=Co, Ni, Cu) clusters were considered as a model of bimetallic particles; (AuSCH<sub>3</sub>)<sub>4</sub> and (AuSCH<sub>2</sub>CHSCH<sub>3</sub>)<sub>4</sub> complexes were considered as a model of thiolate/dithiolate protected clusters. The DFT/PBE method and SBKJC basis set were applied. PRIRODA program on the Lomonosov Moscow State University supercomputer were used [2].

According to calculation the doping of Cu, Co, Ni atoms into the Pt<sub>13</sub> cluster reduces the activation energy of the oxygen dissociation. The most favorable coordination of O<sub>2</sub> and CO on the clusters is platinum atom, not X atom. It can be assumed that the role of doping atom is to change the electronic properties of the monometallic cluster. The CO oxidation on Pt<sub>13</sub> proceeds via the carbonate intermediate, while process proceeds on Pt<sub>12</sub>X through intermediate in which the O – O bond is broken.

O<sub>2</sub> and CO are weakly activated on (AuSCH<sub>3</sub>)<sub>4</sub> cyclic thiolate gold complex, but react with dithiolate gold complex. CO oxidation on (AuSCH<sub>2</sub>CHSCH<sub>3</sub>)<sub>4</sub> proceeds with low activation energies.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 17-03-00962 and 18-33-00431.

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University.

### References:

- [1] R.J. Baxter, P.J. Hu Chem. Phys. 116 (2002) 4379.
- [2] V. Sadovnichy, A. Tikhonravov, Vl. Voevodin, V. Opanasenko "Lomonosov": Supercomputing at Moscow State University. In Contemporary High Performance Computing: From Petascale toward Exascale (Chapman & Hall/CRC Computational Science), Boca Raton, USA, CRC Press (2013) 283.

**CO Oxidation on the Model Pd-Au/HOPG Catalysts: NAP XPS and MS Study**

Bukhtiyarov A.V.<sup>1</sup>, Prosvirin I.P.<sup>1</sup>, Mamatkulov M.<sup>1</sup>, Yudanov I.V.<sup>1,2</sup>, Klyushin A.Yu.<sup>3</sup>,  
Knop-Gericke A.<sup>3</sup>, Neyman K.M.<sup>4,5</sup>, Bukhtiyarov V.I.<sup>1</sup>

*1 – Boreskov Institute of Catalysis, Novosibirsk, Russia*

*2 – Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center  
“Krasnoyarsk Scientific Center SB RAS”, Krasnoyarsk, Russia*

*3 – Fritz-Haber-Institute der Max Planck Society, Berlin, Germany*

*4 – Departament de Ciència de Materials i Química Física and Institut de Química Teòrica i  
Computacional, Universitat de Barcelona, Barcelona, Spain*

*5 – ICREA (Institució Catalana de Recerca i Estudis Avançats), Barcelona, Spain  
avb@catalysis.ru*

Bimetallic systems attract the great interest of many scientific groups due to its ability to induce the significant improvement of catalytic properties compared to monometallic catalysts [1-2]. One of the most frequently studied bimetallic systems is the Pd-Au catalysts due to their high catalytic activity in a number of industrially important reactions. Although a large number of studies of Pd-Au systems have been published in recent years, the reasons of synergistic effects in different catalytic reactions have not been rationalized yet.

One of the most evident proposals, which have been supported by many researchers, is the key role of surface composition of bimetallic catalysts. It is well known that not only the ratio of the introduced metals, but also temperature of calcination will affect the surface composition causing the essential difference between Au/Pd atomic ratios in the bulk and surface [1-2]. It is also evident that surface composition can be varied under the influence of reaction mixture due to enrichment of the surface with one of the metals. Thus the detailed study of surface structure and composition of bimetallic Pd-Au catalysts is necessary to understand the nature of active sites and help to optimize the catalyst composition for the best activity, selectivity and stability.

Success in such a study is impossible without development of procedures for synthesis of bimetallic Pd-Au catalysts with controlled particle size and Au/Pd ratio. Furthermore, low loading of the active metals (< 1-2 wt.%) in high surface area supported catalysts limits the application of surface sensitive techniques. Application of model catalysts, where metal particles deposited on a planar support, could help to get more reliable data concerning surface structure and chemical composition of active metals depending on different treatments [3-4].

Formation of the model bimetallic Pd-Au/HOPG (highly oriented pyrolytic graphite) catalysts has been investigated with XPS and STM [3]. Initially, model “core-shell” type Pd-Au/HOPG catalysts with similar particle size distribution (5–8 nm) were prepared. Subsequent

## OP-4

annealing of these samples in temperature range of 300–400°C leads to formation of Pd–Au alloyed particles.

The prepared Pd-Au/HOPG catalysts were investigated in CO oxidation with combination of NAP XPS and MS techniques. The samples have shown catalytic activity at temperatures above 150°C. The redistribution of Au and Pd on the surface depending on the reaction conditions has been demonstrated. The Pd enrichment of the bimetallic particles surface under reaction mixture has been shown. Apparently CO adsorption induces the Pd segregation on the surface. Under reaction conditions ( $T > 150^{\circ}\text{C}$ ) decomposition of Pd-CO species with simultaneous Pd-Au alloy formation on the surface takes place. In inactive state of the catalyst (after cooling down back to RT) reversible Pd segregation due to Pd-CO formation has been observed. It has been shown that the *in situ* studies are necessary for the investigation of the active sites in Pd-Au bimetallic systems.

Density functional calculations combined with calculations using topological energy expression method (TOP method) were applied to reveal the mechanism of this phenomenon and to quantify the stability of different arrangements of metal atoms in bimetallic PdAu nanoparticles in the presence of CO adsorbate. According to results of this computational approach, adsorption of CO already at a rather moderate coverage is sufficient to make energetically feasible segregation of Pd at terraces of PdAu nanoparticles similar in size with experimentally studied ones.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 14-13-12345.

### References:

- [1] C.W. Yi, K. Luo, T. Wei, D.W. Goodman, *J. Phys. Chem. B.*, 109, 18535 (2005).
- [2] A. Wang, X.Y. Liu, C.-Y. Mou, T. Zhang, *J. Catal.*, 308, 258 (2013).
- [3] A.V. Bukhtiyarov, I.P. Prosvirin, V.I. Bukhtiyarov, *Appl. Surf. Sci.*, 367, 214 (2016).
- [4] A.V. Bukhtiyarov, R.I. Kvon, A.V. Nartova, V.I. Bukhtiyarov, *Russian Chem. Bull.*, 60, 1977 (2011).

## Atomic Ordering in Bimetallic Pd-Au Nanoparticles: Computational Study of Pd Surface Segregation in Reactive Environment

Mamatkulov M.I.<sup>1</sup>, Yudanov I.V.<sup>1,2</sup>, Neyman K.M.<sup>3,4</sup>

*1 – Boreskov Institute of Catalysis, Novosibirsk, Russia*

*2 – Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia*

*3 – Universitat de Barcelona, Barcelona, Spain*

*4 – Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain*

*mikhail@catalysis.ru*

Metal alloys are subject to intensive research because by their catalytic properties they can be superior to pure metals. By changing the ratio of two metals, the catalytic properties of nanoalloys can be adjusted. Besides improving the catalytic performance, the addition of a second metal to the supported catalyst can improve other properties. For example, the addition of palladium to gold nanoparticles, used as a catalyst for the oxidation of CO, increases their thermal stability and, as a result, their lifetime. However, the mechanism of catalysis on nanoalloys can be more complicated than on monometallic catalysts. The task of determining the structure of the bimetallic catalyst is very challenging due to a large variety of possible atomic configurations. Moreover, the structure of the bimetallic nanocatalyst may change under reaction conditions, becoming a dynamic characteristic. A remarkable example of the dynamical restructuring at the nanoscale was reported in a recent experimental study of CO oxidation on palladium-gold model catalysts [1] where reaction was found to proceed only at temperatures above 150 °C and the effect was attributed to migration of palladium to the surface caused by the interaction with adsorbates.

To investigate how thermodynamics of Pd-Au nanoalloy changes under CO adsorption, we performed a computational study applying a theoretical approach, TOP method [2, 3], which combines DFT calculations, to obtain energetic descriptors of a bimetallic nanoalloy, with Monte-Carlo (MC) simulations, to search for the thermodynamically most stable distribution of bimetallic components within nanoparticles of a given shape and size. This combined DFT-MC technique allows us to cover the size range of interest for synthesis of practical nanosystems otherwise hardly tractable by the conventional DF approach. Generating the energy descriptors for particles with the size about 2 nm (200 atoms) we expand the structural analysis to particles with the size of 3-5 nm.

Our calculations indicate that in vacuum the outer shell of Pd-Au nanoalloy is principally composed of gold while the core is a mixture of palladium and gold atoms. However, in the presence of CO the structures with Pd located at the facets of bimetallic particles become energetically favorable [4]. According to DF and TOP-method calculations adsorption of CO already at coverage below 0.3 per surface Pd atom is sufficient to thermodynamically stabilize the structure with (111) terraces of particles completely occupied by Pd. These theoretical

## OP-5

results imply that the stronger (compared to Au) interaction of Pd with adsorbed CO is the driving force for surface segregation of Pd found experimentally [4].

**Acknowledgement.** Calculations were performed using equipment of Siberian Supercomputer Center of Russian Academy of Sciences, HPC computing resources at Lomonosov Moscow State University and Red Española de Supercomputación.

### References:

- [1] A. V. Bukhtiyarov, I. P. Prosvirin, A. A. Saraev, A. Y. Klyushin, A. Knop-Gericke, V. I. Bukhtiyarov, *Faraday Discuss.* 208 (2018) 255.
- [2] S. M. Kozlov, G. Kovács, R. Ferrando, K. M. Neyman, *Chemical Science* 6 (2015) 3868.
- [3] G. Kovács, S. M. Kozlov, K. M. Neyman, *The Journal of Physical Chemistry C* 121 (2017) 10803.
- [4] M. Mamatkulov, I. Yudanov, A. Bukhtiyarov, I Prosvirin, V. Bukhtiyarov, K. Neyman, *The Journal of Physical Chemistry C*, doi: 10.1021/acs.jpcc.8b0740 (2018).



## Insights into Fundamental Aspects of Au Catalysis from Operando and In Situ Spectroscopy: Methanol Synthesis on Au/ZnO as a Key Example

Wiese K.<sup>1</sup>, Rezvani A.<sup>1</sup>, Abdel-Mageed A.M.<sup>1</sup>, Klyushin A.<sup>2</sup>,  
Knop-Gericke A.<sup>2</sup>, Schlögl R.<sup>2</sup>, Behm R.J.<sup>1</sup>

1 – Institute of Surface Chemistry and Catalysis, Ulm University, Ulm, Germany

2 – Fritz-Haber-Institute, Department of Inorganic Chemistry, Berlin, Germany

juergen.behm@uni-ulm.de

The high activity and selectivity of supported Au catalysts already under mild reaction conditions in a wide range of oxidation and reduction reaction has motivated extensive research efforts for over three decades.[1] As one example, Au/ZnO catalysts have been identified as highly active, selective and stable catalysts for ‘green’ methanol synthesis from CO<sub>2</sub> (CO<sub>2</sub> + H<sub>2</sub> => CH<sub>3</sub>OH + H<sub>2</sub>O) under reaction conditions ranging from close to ambient up to industrially applied pressures. [2] This reaction is not only environmentally attractive, but also of interest for chemical energy storage, if excess electric energy from renewable energy sources is used for generating H<sub>2</sub> via electrolysis of water.[3]

In the present contribution we report on the role of reaction induced changes of the structural and electronic properties of Au/ZnO for reaction under industrial and idealized conditions, employing a combination of kinetic and time resolved *in situ* / *operando* spectroscopies such as high-pressure *operando* FTIR (DRIFTS), near ambient pressure X-ray photoelectron (NAP-XPS) and X-ray absorption spectroscopy (XAS) at the O K-edge, in addition to temporal analysis of products (TAP) measurements.

*Operando* DRIFTS measurements performed at pressures between 1 and 50 bar revealed that CO, which is formed during methanol synthesis via the RWGS reaction (CO<sub>2</sub> + H<sub>2</sub> => CO + H<sub>2</sub>O), adsorbs primarily on sites typical for metallic or negatively charged gold species (CO<sub>ad</sub>@Au<sup>δ-</sup>).[4,5] The intensity of the band at 2078 cm<sup>-1</sup>, which is related to the CO<sub>ad</sub>@Au<sup>δ-</sup> species and hence to their coverage, closely follows the methanol formation rate during an initial activation phase, until reaching steady-state conditions. Furthermore, NAP-XPS and XAS (O K-edge) measurements point to a close correlation between i) the formation of O-vacancies (defects) on the ZnO support during reaction, ii) the methanol formation rate, and iii) the CO<sub>ad</sub> coverage on the Au<sup>δ-</sup> species. In addition, transient experiments between CO<sub>2</sub>/H<sub>2</sub> and CO/H<sub>2</sub> gas mixtures performed at 5 bar indicated that the O-vacancies are predominantly created by reaction with CO, while CO<sub>2</sub> can partially replenish these vacancies.[5]

These results were corroborated by TAP reactor measurements.[6] Exposing a pre-reduced Au/ZnO catalyst to a sequence of CO<sub>2</sub> pulses and then titrating the amount of active oxygen on the surface by another sequence of CO pulses,[7] we found that CO<sub>2</sub> can replenish the O-vacancies. Hence, there seems to be a dynamic equilibrium between the creation of O-vacancies during reaction, either by CO generated via the RWGS or by the interaction with H<sub>2</sub>,

## OP-6

and their replenishment by CO<sub>2</sub>. This results in a steady-state concentration of O-vacancies and hence in a partial negative charging of the Au nanoparticles during this reaction, which can sensitively affect or even determine the activity of Au/ZnO in this reaction.

The close correlation between oxygen vacancy concentration and Au charging state on the one hand and the catalytic performance of the catalyst was derived also from time-resolved kinetic measurements, changing from reaction in a H<sub>2</sub>/CO<sub>2</sub> mixture to a CO/H<sub>2</sub> mixture and back again. This revealed a high initial reaction rate on the catalyst after reaction in the strongly reductive CO/H<sub>2</sub> mixture, which then decays to the typical rate in CO/H<sub>2</sub>. Apparently, the higher concentration of O-vacancy sites after exposure to a CO/H<sub>2</sub> mixture, which was identified also spectroscopically, gives rise to a further enhanced activity. This, however, is transient due to the partial replenishment of the O-vacancies upon exposure to the H<sub>2</sub>/CO<sub>2</sub> mixture.

Finally, CO adsorption DRIFTS measurements indicate that after the O400 pretreatment the Au nanoparticle surface is hardly accessible for CO adsorption, which would be consistent with a partial overgrowth of the Au nanoparticles by a ZnO layer under these conditions. This conclusion is supported also by high-resolution electron microscopy (HR-TEM) measurements, performed after pretreatment and after subsequent methanol reaction (1000 min at 5 bar). Such structural modifications resemble reports for Cu/ZnO catalyst.[8]

In total, these results demonstrate a close correlation between the formation/replenishment of O-vacancies in the ZnO support, the charge state of the Au nanoparticles and the methanol formation activity from CO<sub>2</sub>/H<sub>2</sub>. Similar trends and effects are suggested to apply also for this reaction on the commercial Cu/ZnO catalysts.

**Acknowledgement.** We thank the Helmholtz-Zentrum Berlin (HZB) for the allocation of beamtime at the ISSS beamline at BESSY-II.

### References:

- [1] M. Haruta, *Catal. Surv. Jap.* 1 (1997) 61.
- [2] Y. Hartadi et al., *J. Catal.* 333 (2016) 38.
- [3] R. Schlögl, *Angew. Chem. Int. Ed.* 54 (2015) 2.
- [4] X. Liu et al., *J. Am. Chem. Soc.* 134 (2012) 10251.
- [5] A. M. Abdel-Mageed et al., *Angew. Chem. Int. Ed.*, online available, DOI: 10.1002/anie.201900150.
- [6] D. Widmann and R. J. Behm, *Acc. Chem. Res.* 47 (2014) 740.
- [7] K. Wiese et al., *Catal. Today*, online available, DOI: 10.1016/j.cattod.2018.11.074.
- [8] T. Lunkenbein et al., *Angew. Chem. Int. Ed.* 54 (2015) 4544.

## The Investigation of Thermal Decomposition of Heterobimetallic PtZn(CH<sub>3</sub>COO)<sub>4</sub> Acetate Complex in Reductive Conditions by *In Situ* XAFS

Smirnova N.S.<sup>1</sup>, Khramov E.V.<sup>2</sup>, Stolyarov I.P.<sup>1</sup>, Cherkashina N.V.<sup>1</sup>, Baeva G.N.<sup>3</sup>,  
Bragina G.O.<sup>3</sup>, Yakushev I.A.<sup>1</sup>, Mashkovsky I.S.<sup>3</sup>, Vargaftik M.N.<sup>1</sup>, Stakheev A.Yu.<sup>3</sup>

1 – N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
Moscow, Russia

2 – National Research Center «Kurchatov Institute», Moscow, Russia

3 – N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia  
felisine@gmail.com

The supported bimetallic platinum-zinc catalytic systems are considered as promising catalysts for a plenty of important processes, such as selective hydrogenation [1, 2] and dehydrogenation reactions, steam reforming of methanol [3], etc. The superior catalytic properties of PtZn are explained in terms of intermetallic compound formation. Such bimetallic catalysts are commonly prepared from the solutions of individual salts followed by high-temperature reduction. The main disadvantage of this method is formation of very large particles and mixed phases. Another approach to prepare efficient intermetallic catalyst involves the use of heterobimetallic acetate complexes as precursors. Thermolysis of these compounds in mild conditions produces the bimetallic phase with predetermined composition.

In this work we investigated the thermal decomposition of the complex PtZn(CH<sub>3</sub>COO)<sub>4</sub>(H<sub>2</sub>O)(CH<sub>3</sub>COOH)<sub>2</sub> in reductive atmosphere to find the optimum conditions for formation of the bimetallic PtZn nanoparticles. According to *in situ* XAFS, the decomposition of unsupported PtZn acetate complex starts from 100°C with formation of metallic platinum, while zinc remains in oxygen environment (fig.1). The structure rearrangement of Pt fcc lattice to tetragonal PtZn intermetallic phase occurs after complete zinc reduction (~275°C). After 300°C only an increase in particle size of PtZn nanoparticles is observed.

Based on these data, the optimum temperature (300°C) for the preparation of bimetallic Pt-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst was selected. The obtained supported sample showed high activity in the model reaction of selective diphenylacetylene hydrogenation.

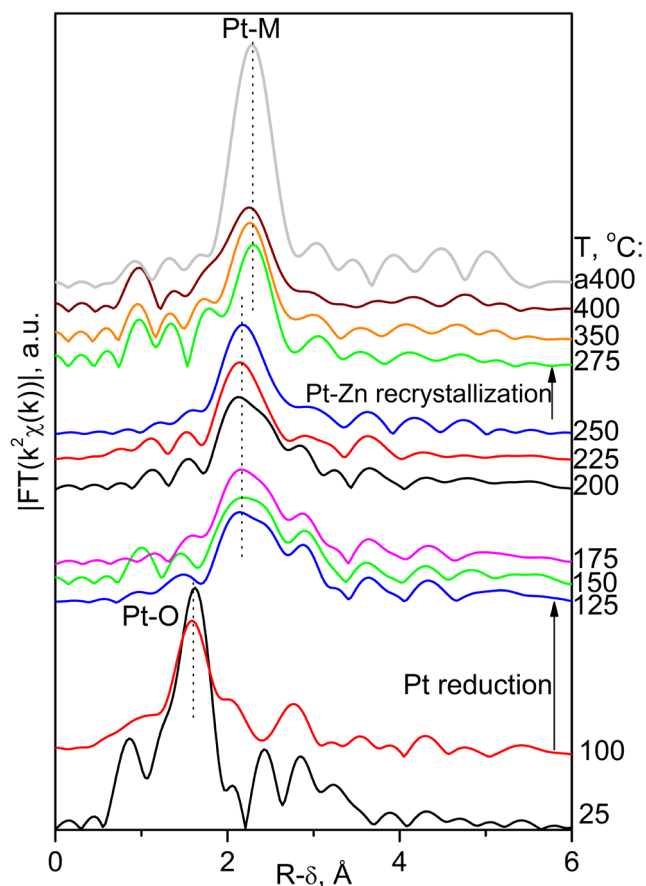


Fig.1. *In situ* Pt<sub>LIII</sub> EXAFS of PtZn(OAc)<sub>4</sub> during its thermal decomposition in 5%H<sub>2</sub>/He flow

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research, grants № 18-33-00632, 18-03-00228.

**References:**

- [1] M. Consonni, D. Jokic, D. Yu Murzin, R. Touroude, J. Catal. 188 (1999) 165.
- [2] S. Iihama, S. Furukawa, T. Komatsu, ACS Catal. 6 (2016) 742.
- [3] A.P. Tsai, S. Kameoka, K. Nozawa, M. Shimoda, Y. Ishii, Acc. Chem. Res. 50 (2017) 2879.

## On the Electronic and Geometric Structure of a Single Atom Cu/UiO-66 Catalyst during CO Oxidation: An Operando FTIR and XAFS Study

Abdel-Mageed A.M.<sup>1</sup>, Fauth C.<sup>1</sup>, Rungtaweeworant B.<sup>2</sup>, Yaghi O.M.<sup>2</sup>, Behm R.J.<sup>1</sup>

<sup>1</sup> – Institute of Surface Chemistry and Catalysis, Ulm University, Ulm, Germany

<sup>2</sup> – Department of Chemistry, University of California, Berkeley, California, USA

ali.abdel-mageed@uni-ulm.de

Metal-organic frameworks (MOFs) have emerged as highly promising microporous materials with intriguing properties for various applications, including heterogeneous catalysis.[1] Since they allow to precisely tailor and control the electronic properties and local environment of the active site(s), their reactivity can be sensitively tuned for a variety of oxidation and reduction reactions.[2] Recently, we succeeded in covalently anchoring individual Cu atoms at defect sites of the Zr-oxide clusters in the UiO-66 MOF, a Zr-based MOF ( $Zr_6O_4(OH)_4(BDC)_6$  (BDC = 1,4-benzene-dicarboxylate)).[3,4]

Using CO oxidation as a model reaction, we examined the catalytic performance and stability of the Cu metalated UiO-66 single atom catalyst in the temperature range between 80 and 250°C under idealized and realistic reaction conditions,[5] trying to identify the chemical nature and structure of the active Cu species under up to realistic reaction conditions. Kinetic measurements were combined with a number of spectroscopic and structural characterization techniques, including *operando* XAFS and FTIR spectroscopy, together with high resolution electron microscopy measurements.

Kinetic measurements in a CO/O<sub>2</sub> (1:1) gas mixture, performed after reductive pretreatment (10% H<sub>2</sub>/N<sub>2</sub>; 1 h, 250°C) of the Cu@UiO-66 catalyst, showed that the activity increases slowly from 3.4 to 6.5  $\mu\text{mol}_{\text{CO}_2} \text{g}_{\text{Cu}}^{-1} \text{s}^{-1}$  between 80°C and 150°C. From 150°C to 250°C the increase was much more pronounced, reaching 350  $\mu\text{mol}_{\text{CO}_2} \text{g}_{\text{Cu}}^{-1} \text{s}^{-1}$  at 250°C. Time-dependent measurements at 250°C revealed a stable activity, with no measurable deactivation over 1500 min. Time-resolved diffuse reflectance FTIR (DRIFTS) measurements, performed at temperatures between 80°C and 250°C, indicated that CO adsorbs as mono-carbonyl species on Cu atoms with the wavenumber depending on the oxidation state of the Cu species. XANES measurements performed at the Cu K-edge (8979 eV) showed that after pretreatment Cu exists mainly as Cu<sup>1+</sup>, while during the subsequent CO oxidation at 250°C a gradual transformation of Cu<sup>1+</sup> to Cu<sup>2+</sup> occurs, reaching an approximate composition of 20±5 % Cu<sup>1+</sup> and 75±5 % Cu<sup>2+</sup> after 380 min on stream. The dominance of Cu<sup>2+</sup> during reaction was confirmed by XPS measurements after reaction, which revealed a strong Cu 2p satellite peak characteristic for Cu<sup>2+</sup>. [6] Based on EXAFS measurements, Cu is predominantly bound to oxygen, e.g., in OH groups or carboxylates, both after reduction in H<sub>2</sub> and during CO oxidation. An average Cu-O coordination number of 1.4 ± 0.3 was detected after reductive pretreatment, which increased to 2.1 ± 0.4 during CO oxidation, with a Cu-O bond distance of 1.95 ± 0.02 Å

## OP-8

in both cases.[7] In addition, the Fourier transformed EXAFS data indicate the absence of any contributions from a Cu-Cu scattering shell, e.g., at Cu-Cu distances of  $\sim 2.67$  Å (metallic Cu) or 3.2-3.4 Å (CuO or Cu<sub>2</sub>O). These findings point to the presence of Cu species in an atomically dispersed state and exclude the presence of any Cu<sub>x</sub> or CuO<sub>x</sub> clusters or nanoparticles. This conclusion is confirmed also by results of HAADF-STEM measurements, which only resolved highly dispersed atomic Cu species, both in fresh Cu@UiO-66 and after subsequent reaction.

Finally, results of DFT computations guided by experimental findings helped to clarify the local structure and bonding situation of these single Cu sites in the Cu/UiO-66. Here the Cu/UiO-66 catalyst was modelled by anchoring Cu at OH<sup>-</sup>/H<sub>2</sub>O ligands, capping the defect sites of UiO-66 (missing terephthalic acid anion species) with Cl<sup>-</sup> as a ligand. In the resulting optimized structure for the fresh sample the Cu<sup>1+</sup> ions are threefold coordinated, binding to two oxygen atoms (oxygen containing ligands) and one chlorine atom at bond distances of Cu–O = 1.89 and 1.95 Å and Cu–Cl = 2.15 Å, respectively. After H<sub>2</sub> pretreatment we assumed that Cu is twofold coordinated, binding to OH<sup>-</sup>/H<sub>2</sub>O of neighbored Zr oxide clusters, while the Cl ligand is removed. The optimized structure of Cu–UiO-66 shows Cu–O bond distances of 1.86 Å, in good agreement with the EXAFS results. These spectroscopic and structural results will be discussed together with additional findings from temporal analysis of products (TAP) measurements in a mechanistic picture of the CO oxidation reaction on these catalysts.

**Acknowledgement.** We thank the Deutsche Elektronen-Synchrotron (DESY) facility in Hamburg (Germany) as well as the Elettra Sincrotrone Trieste (Italy) for the allocation of beamtime at the P65 beamline (Petra III extension) and XAFS beamline, respectively.

### References:

- [1] H. Furukawa et al., *Science*, 341 (2013) 1230444.
- [2] B. Rungtaweeworanit et al., *Nano. Lett.* 16 (2016) 7642.
- [3] J. H. Cavka et al., *J. Am. Chem. Soc.* 130 (2008) 13850.
- [4] K. M. Choi et al., *J. Am. Chem.* 139 (2017) 356.
- [5] A. M. Abdel-Mageed, *J. Am. Chem. Soc.* 141 (2019) 5201.
- [6] G. Wu et al., *Catal. Sci. Technol.* 1 (2011) 601.
- [7] F. Giordanino et al., *Dalton Trans.* 42 (2018) 12741.

## NAP XPS Study of CO Oxidation over CuFeAl Nanocomposite Catalysts

Saraev A.A.<sup>1</sup>, Tsapina A.M.<sup>1</sup>, Selivanova A.V.<sup>1</sup>, Fedorov A.V.<sup>1</sup>,  
Vorokhta M.<sup>2</sup>, Šmíd B.<sup>2</sup>, Kaichev V.V.<sup>1</sup>

1 – Boreskov Institute of Catalysis, Novosibirsk, Russia

2 – Charles University, Prague, Czech Republic

asaraev@catalysis.ru

Fe-based catalysts have been the subject of intense research in the past due to a wide application in various fields, such as water-gas shift reactions, the Fisher-Tropsch synthesis, partial oxidation of H<sub>2</sub>S, and ammonia synthesis. Recently, it has been showed that the Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts demonstrate moderate activity in the oxidation of CO [1]. Moreover, their activity could be increased by promotion with copper. These catalysts are inexpensive and environmentally friendly that allow using theirs for catalytic combustion of non-traditional fuels such as peat, lignite, wood or food waste, sewage sludge, and the other industrial wastes. The Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP XPS) was used to study the chemical states and the relative concentrations of elements on the surface of the catalysts directly under the reaction conditions. The NAP XPS study was performed at Charles University in Prague, Czech Republic. The experiments were performed on a photoelectron spectrometer (Specs Surface Nano Analysis, GmbH Germany) equipped with DeviSim reaction cell. The powder of the catalyst was deposited on a stainless steel mesh attached to a special sample holder. The catalyst of optimal composition (5 wt% of CuO, 78 wt% of Fe<sub>2</sub>O<sub>3</sub>, and 17 wt% of Al<sub>2</sub>O<sub>3</sub>) and reference CuO and CuFe<sub>2</sub>O<sub>4</sub> samples were investigated in a flow of CO and a flow of mixture of CO and O<sub>2</sub> (2:1) in the temperatures ranging from room temperature to 600°C at the pressure of 1 mbar.

*In situ* XPS study allows us to determine the reduction temperature of copper and iron and phase transitions occurring in the CuFeAl nanocomposite catalyst, CuO and CuFe<sub>2</sub>O<sub>4</sub> under the reaction conditions. There was found that the reduction of the copper cations in the catalyst and CuO to metallic state proceeds with formation of Cu<sup>1+</sup> state when in the CuFe<sub>2</sub>O<sub>4</sub> – without formation of Cu<sup>1+</sup> state. The presence of alumina in the catalyst leads to increase the reduction temperature of copper and iron. In case of catalysts the addition of oxygen to gas mixture leads the reduction of copper from Cu<sup>2+</sup> to Cu<sup>1+</sup> and no any copper in the metallic state was observed even at 500°C. These facts allow us to speculate that CO oxidation over CuFeAl nanocomposite catalysts could proceed via redox Mars-Van Krevelen mechanism. The ability to reduce copper at low temperatures increases the catalytic activity of the CuFeAl nanocomposite catalysts in the oxidation of CO.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 17-73-20157.

### Reference:

[1] A.V. Fedorov, A.M. Tsapina, O.A. Bulavchenko, A.A. Saraev, G.V. Odegova, D.Yu. Ermakov, Y.V. Zubavichus, V.A. Yakovlev, V.V. Kaichev, Catal. Lett. 148 (2018) 3715.

## In Situ XRD and XPS Study of the Reduction Process of Mixed Mn-Zr Oxide Catalysts of CO Oxidation

Bulavchenko O.A.<sup>1,2</sup>, Vinokurov Z.S.<sup>1,2</sup>, Afonasenko T.N.<sup>1</sup>, Tsyriľ'nikov P.G.<sup>3</sup>, Saraev A.A.<sup>1,2</sup>,  
Kaichev V.V.<sup>1,2</sup>, Tsybulya S.V.<sup>1,2</sup>

1 – Boreskov Institute of Catalysis, Novosibirsk, Russia

2 – Novosibirsk State University, Novosibirsk, Russia

3 – Center of New Chemical Technologies BIC, Omsk, Russia  
isizy@catalysis.ru

Mn-containing oxides can effectively catalyze the oxidation of CO, hydrocarbons and chlorocarbons. On manganese oxides, oxidation reactions are known to proceed through the Mars-van Krevelen mechanism, according to which in the first step lattice oxygen oxidizes the substrate which is accompanied by generation of an oxygen vacancy, and in the second step the reduced catalyst is reoxidized by gas-phase molecular oxygen. Under these considerations, the catalytic activity is significantly determined by the redox properties of the oxides. Cooperative utilize of Mn and zirconia leads to synergetic effect – increase in catalytic activity as compared with simple oxides. In double metal oxide catalysts, not only simple compounds are present in system, but the formation of mixed oxides is possible. Mn cations can enter the lattice of ZrO<sub>2</sub> with the formation of solid solutions Zr<sub>1-x</sub>Mn<sub>x</sub>O<sub>2</sub>, in which lattice oxygen possesses sufficiently high mobility and hence high reactivity. On the other hand, some authors suppose that the active species in oxidation reactions is mobile oxygen that is incorporated in disperse MnO<sub>x</sub> rather than lattice oxygen of the solid solution. Moreover, in a reducing atmosphere, a segregation of manganese with the formation of dispersed MnO<sub>x</sub> is possible on the surface of the solid solution Zr<sub>1-x</sub>Mn<sub>x</sub>O<sub>2</sub>.

A series of mixed MnO<sub>x</sub>-ZrO<sub>2</sub> catalysts with different molar ratios Mn/Zr have been prepared by coprecipitation. The effect of the calcination temperature and composition of the MnO<sub>x</sub>-ZrO<sub>2</sub> system on its structural characteristics and catalytic properties in the reaction of CO oxidation was studied. According to XRD and TPR-H<sub>2</sub> data, an increase in the calcination temperature of Mn<sub>0.12</sub>Zr<sub>0.88</sub>O<sub>2</sub> from 450 to 900°C caused a structural transformation of the system accompanied by the decomposition of solid solution with the release of manganese ions from the structure of ZrO<sub>2</sub> and the formation of, initially, highly dispersed MnO<sub>x</sub> particles and then a crystallized phase of Mn<sub>3</sub>O<sub>4</sub>. The dependence of the catalytic activity of MnO<sub>x</sub>-ZrO<sub>2</sub> in the reaction of CO oxidation on the calcination temperature takes an extreme form. A maximum activity was observed after heat treatment at 650–700°C, i.e., at limiting temperatures for the occurrence of a solid solution of manganese ions in the cubic modification of ZrO<sub>2</sub>.

The characteristics of mixed Mn-Zr oxides with different molar ratios Mn/Zr (0.1-9) calcined at 650°C have been investigated. It has been found that at concentration of Mn below 30 at%, the samples are single-phase solid solutions (Mn<sub>x</sub>Zr<sub>1-x</sub>O<sub>2-δ</sub>) based on a ZrO<sub>2</sub> structure.



## OP-10

X-ray photoelectron spectroscopy measurements showed that manganese in these solutions exists mainly in the  $Mn^{4+}$  state on the surface. An increase in the Mn content mostly leads to an increase in the number of Mn cations in the structure of solid solutions, however a part of manganese forms  $Mn_2O_3$  and  $Mn_3O_4$  in crystalline and amorphous states. The samples of  $Mn_{0.4}Zr_{0.6}O_2$ – $Mn_{0.6}Zr_{0.4}O_2$  exhibited a maximum catalytic activity in CO oxidation. The origin of active sites can be related to the presence of the highly dispersed  $MnO_x$  particles, which were not the solid solution constituents, or formation of the  $Mn_xZr_{1-x}O_{2-\delta}$  solid solution.

One of the main ways to study redox properties of different oxides is a temperature-programmed reduction (TPR- $H_2$ ) technique. On the basis of its results, it is possible, for example, to draw some conclusions about the presence of various forms of manganese oxides. However, TPR is an indirect method that allows monitoring only the absorption of hydrogen rather than the change in structural characteristics of catalysts and in the charge state of Mn and Zr cations. To obtain detailed information on various stages of the reduction of Mn-Zr mixed oxides, the study was carried out using a combination of methods: temperature-programmed reduction, X-ray diffraction, and X-ray photoelectron spectroscopy. The reduction of these oxides with hydrogen was studied by a TPR- $H_2$ , in situ XRD, and near ambient pressure XPS in a temperature range from 100 to 650 °C. It was shown that the reduction of the solid solutions  $Mn_xZr_{1-x}O_{2-\delta}$  proceeds via two stages. During the first stage, between 100 and 500 °C, Mn cations incorporated into the solid solutions  $Mn_xZr_{1-x}O_{2-\delta}$  undergo the partial reduction. During the second stage, at temperatures between 500 and 700 °C, Mn cations segregate on the surface of solid solution. In the samples with more than 30 at% Mn, the reduction of manganese oxide was observed:  $Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ .

Catalysts with higher catalytic activity ( $Mn_{0.4}Zr_{0.6}O_2$ – $Mn_{0.6}Zr_{0.4}O_2$ ) consist of solid solution with higher Mn content. Appearance of crystalline Mn oxide leads to drop in catalytic properties ( $Mn_{0.7}Zr_{0.3}O_2$  -  $Mn_{0.9}Zr_{0.1}O_2$ ). The origin of low-temperature TPR peak is discussed in the literature. Our study shown that the first TPR peak is associated with the reduction of Mn cations in the bulk of solid solution, rather than the amorphous or disperse  $MnO_x$ . Therefore, high activity of  $Mn_{0.4}Zr_{0.6}O_2$ – $Mn_{0.6}Zr_{0.4}O_2$  catalysts is related to formation of the  $Mn_xZr_{1-x}O_{2-\delta}$  solid solution with highest Mn content and high oxygen mobility.

### References:

- [1] O.A. Bulavchenko, Z.S. Vinokurov, T.N. Afonassenko, P.G. Tsyurul'nikov, S.V. Tsybulya, A.A. Saraev, V.V. Kaichev, Dalton Trans, 44 (2015) 15499.
- [2] T.N. Afonassenko, O.A. Bulavchenko, T.I. Gulyaeva, S.V. Tsybulya, P.G. Tsyurul'nikov Kinet. Catal. 59 (2018) 104.

## OP-11

### Manganese Oxides under OER

Skorupska K., Jone D.T., Mom R., Sulzmann F., Chuang Ch.-H., Melder J., Kurz P.,  
Knop-Gericke A., Schlögl R.

*Fritz-Haber-Institut of of the Max-Planck Society, Berlin, Germany*  
*skorupska@fhi-berlin.mpg.de*

We present a study on manganese oxides during and after oxygen evolution (OER). The analysis was based on results obtained by synchrotron based soft X-ray spectroscopy. The Mn L- and O K- absorption edges were recorded. The dipole selection rule allows us to probe the empty 3d states of Mn (2p 3d excitation) and the empty O 2p orbitals (1s 2p excitation). This approach gives the opportunity to monitor changes (under applied potential) in the oxidation state of Mn and the Mn 3d/O 2p hybridization.

We compare the in-situ results wherein electrochemical and spectroscopic experiments were performed simultaneously with ex-situ obtained results for standard manganese oxides. We will try to draw conclusions concerning the manganese oxidation state, covalence and active phase of manganese oxide.

### Modular Concept for Catalysis Research at BESSY from an Engineer Point of View

Stotz E.<sup>1</sup>, Hävecker M.<sup>1,2</sup>, Valsco-Velez J.J.<sup>1,2</sup>, Knop-Gericke A.<sup>1,2</sup>, Schlögl, R.<sup>1,2</sup>

*1 – Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany*

*2 – Max-Planck-Institute for Chemical Energy Conversion, Mülheim, Germany  
stotz@fhi-berlin.mpg.de*

In order to meet the requirements of flexible measurement operation the FHI has implemented a modular system to realize different sample environment.

In the past, samples such as pellets and single crystals were attached to a sapphire sample holder which had to be transferred to the measuring chamber. Other cell assemblies such as reaction cells or electrochemical cells also had to be mounted on the sapphire sample holder. Due to the limited space, the new cells were quite small. As a result, on one hand, manufacturing and assembly was difficult and, on the other hand, the benefits were sometimes very limited.

These limitations led to the development of a new concept. The new modular system enabled the usage of new sample holders and cell setups. The concept was realized by “inlays”, with different variants which will be discussed in my lecture.

Furthermore, the sample environment was considered and implemented in “modules”. The module is an independent stand-alone unit, which equipped with a measuring chamber, a manipulator tube assembly, own gas supply and gas analytics. The module can be used to optimize the reaction parameters prior the XPS measurements. The module is mobile and can be connected to any of the three beamlines (ISIS, EMIL and BEIChem) respectively to the corresponding analyzers.

## Differentiation of Strongly Bound Oxygen on Silver

Sulzmann F.<sup>1</sup>, Carbonio E.<sup>3</sup>, Jones T.<sup>1</sup>, Knop-Gerincke A.<sup>2</sup>, Schlögl R.<sup>1,2</sup>

1 – Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Inorganic Chemistry, Berlin, Germany

2 – Department of Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

3 – Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, BESSY II, Berlin, Germany  
Frederic@fhi-berlin.mpg.de

Understanding the catalytic partial oxidation of methanol to formaldehyde is a long standing problem that is poised to face a resurgence in interest. The current interest in it stems from two main factors:

i) formaldehyde is one of the most important chemicals used in the chemical manufacturing industry. ii) formaldehyde is the building block for polyoxymethylene dimethyl ethers (OME), which are a promising soot free alternative for fossil derived diesel.

Nowadays, formaldehyde is produced industrially by the reaction of methanol over either metal-oxide or silver based catalysts. The two catalysts require different reaction parameters and offer differing selectivity. For example, it is believed that formaldehyde is produced through both a partial oxidation and dehydrogenation pathway over silver based catalysts, while only the former seems to be important for the metal-oxide catalyst. This fact, and the simplicity of the silver based catalyst (modelled catalyst system), motivate our interest in the presented project.

The silver oxygen system has been thoroughly investigated in the last decades, as it is the basis of important large scale, industrial processes; ethylene epoxidation and methanol oxidation. Early on X-ray photoelectron spectroscopy (XPS) proved a powerful tool for such investigations. The state of the art XPS set-up in the 90's consisted of two chambers [1]; a preparation/reaction chamber (1 bar) and an XPS chamber (UHV). With this kind of set-up, it was possible to discriminate between at least three different oxygen species ( $O_\alpha$ ,  $O_\beta$ ,  $O_\gamma$ ) on the silver surface.

These oxygen species were initially found and characterised with TPD based experiments and later further investigated with XPS. The  $O_\alpha$  species (528.7 eV [2]) is known as atomically adsorbed oxygen on a reconstructed silver surface, being stable only under moderate temperatures. In the 90's, it was believed that the  $O_\beta$  species (531.7 eV [2]) can be explicitly attributed to bulk dissolved oxygen. Recently, however, Jones et al. [4] reported that an  $SO_4$  induced surface reconstruction can account for the  $O_\beta$  species prepared under UHV conditions.

Schlögl's group reported of an oxygen species that is stable at high temperatures and labelled it  $O_\gamma$ . This oxygen species, with a binding energy of 529.1 to 529.7 eV [2], is described as subsurface oxygen forming a thin oxide-like-layer on the silver surface. Since silver

## OP-13

undergoes faceting to expose Ag (111), it is stated, that  $O_{\gamma}$  forms only on the (111) facet. Rocha et al. [2] found two oxygen species formed at 500°C in 0.25 mbar of oxygen, one denoted  $O_{\gamma}$  and the other  $O_{\alpha 2}$ . Reichelt et al. [3] later used UHV techniques to show the strongly bound oxygen species could, in some cases, be due to Molybdenumoxide contamination on the silver surface, but the question remains as to the generality of that finding under *in situ* conditions.

We will now report on ways to differentiate between oxygen species attributed to silver and the ones attributed to Molybdenumoxide using synchrotron NAP-XPS in combination with X-ray absorption measurements.

### References:

- [1] X. Bao et al. Surface Science. 1-2 (1993) 284.
- [2] T. Rocha et al. Phys. Chem. Chem. Phys. 14 (2012) 14.
- [3] R. Reichelt et al. J. of Physical Chemistry C 35 (2011) 115.
- [4] T. Jones et al. ACS Catalysis (2018).

## In Situ XPS Study of Selective Methanol Oxidation over Cu Catalysts on the Base of Layered Double Hydroxides

Bukhtiyarova M.V., Prosvirin I.P., Bukhtiyarov A.V., Panafidin M.A.  
*Boreskov Institute of Catalysis, Novosibirsk, Russia*  
*m vb@catalysis.ru*

The industrial production of formaldehyde from methanol is an important chemical process. Formaldehyde polymerize at room temperature and is commercially available as an aqueous solution known as formalin (37 wt%). Formaldehyde may be synthesized industrially by selective oxidation of methanol according to the reaction:  $2\text{CH}_3\text{OH} + \text{O}_2 \rightarrow 2\text{CH}_2\text{O} + 2\text{H}_2$ . The commercial oxidation of methanol is performed with two types of catalysts: silver catalyst or iron molybdate [1]. It was shown [2] that Cu single crystal, Cu foil and Cu powder obtained by reduction of  $\text{Cu}_2\text{O}$  can be also used as catalysts in selective methanol oxidation of methanol to formaldehyde. The usage of Cu catalysts instead of silver ones can decrease the costs of the process. Cu-containing layered double hydroxides can be promising candidates for the reaction. The LDHs, known as hydrotalcite-like compounds, can be represented by general formula:  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$  [3]. The pure hydrotalcite phase can be obtained when  $0.2 < x < 0.33$ , where  $x$  is a ratio of  $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$ ,  $\text{M}^{2+}$  and  $\text{M}^{3+}$  ions can be represented by  $\text{Cu}^{2+}$  and  $\text{Al}^{3+}$  ions respectively.

The aim of this work was combined NAP XPS and MS techniques for investigation of electronic and catalytic properties of Cu catalysts on the base of layered double hydroxides under methanol oxidation reaction. The comparison of the spectroscopic information from the surface with catalytic properties of the sample studied can provide the identification of the oxygen species active in the selective oxidation of methanol [4].

In this work, we studied two samples differed in chemical composition with the molar Cu:Al and Cu:Al:Zn ratios of 1:1 and 1:1:1. The synthesis of layered double hydroxides was performed by the co-precipitation method at a constant pH of  $9.0 \pm 0.1$  and temperature of  $70^\circ\text{C}$ . A mixture of NaOH and  $\text{Na}_2\text{CO}_3$  was used as a precipitation agent. The samples were aged at  $70^\circ\text{C}$  for 4 h. The aged precipitate was filtered, washed with hot water to remove excess of sodium ions, dried at  $110^\circ\text{C}$  for 14 h and calcined at  $450^\circ\text{C}$  for 4 h. Formation of hydrotalcite phase was confirmed by XRD analysis. XRD patterns of the samples dried at  $110^\circ\text{C}$  show the presence of pure hydrotalcite phase. Treatment at  $450^\circ\text{C}$  results in destruction of the hydrotalcite phase and the formation of low-crystalline CuO.

The NAP XPS and MS techniques were combined for investigation of the copper chemical state and catalytic properties of the of Cu catalysts on the base of layered double hydroxides under methanol oxidation reaction.

### References:

- [1] B. Stiles, T.A. Koch, Catalyst Manufacture, New York, 1995.
- [2] H. Werner, D. Herein, G. Schulz, U. Wild, R. Schlögl, Catal. Lett. 49 (1997) 109.
- [3] M.V. Bukhtiyarova, J. Solid State Chem. 269 (2019) 494.
- [4] I.P. Prosvirin, A.V. Bukhtiyarov, H. Bluhm, V.I. Bukhtiyarov, Appl. Surf. Sci. 363 (2016) 303.

## In Situ and Advanced Synchrotron Studies of Catalysts for Bio-Oxygenates Hydroconversion

Alekseeva M.V.<sup>1,2</sup>, Smirnov A.A.<sup>1,2</sup>, Selischeva S.A.<sup>1,2</sup>, Shilov I.N.<sup>1,2</sup>, Fedorov A.V.<sup>1,2</sup>,  
Bulavchenko O.A.<sup>1,2</sup>, Saraev A.A.<sup>1,2</sup>, Yakovlev V.A.<sup>1,2</sup>

1 – Boreskov Institute of Catalysis, Novosibirsk, Russia

2 – Novosibirsk State University, Novosibirsk, Russia

*bykova@catalysis.ru*

A detailed study of the molecular structure of the catalyst is of particular importance to establish the relationship between the nature of its active component/center and catalytic action, regardless of the type of reaction considered. The knowledge gained is a basis for appropriate molecular design of the catalyst, thereby allowing one to run the catalytic process in the right direction. At present, due to the increased interest in alternative sources of energy, the necessity to convert renewable raw materials into valuable products as well as efficient energy recovery are particularly relevant. In such types of catalytic transformations, the participation of the catalyst is imperative, and deep understanding of the relationship between structural features and catalytic action is indispensable. Here, a special role is given to physicochemical approaches, making possible to study the state of the active component, especially under conditions close to the real catalytic process.

This talk will cover a number of studies focused on catalytic processing of renewable raw materials in the presence of heterogeneous catalysts based on transition metals [1-3]. In this cycle of works, special attention is paid to the state of the active phase in various types of Ni, Cu, Fe, and Mo-containing catalysts intended for use in hydroconversion of natural oxygenates. Catalytic hydrotreatment of bio-oil and its model compounds, as well as the selective hydrogenation of furfural into valuable derivatives, such as 2-methylfuran, furfuryl alcohol etc., will be discussed. At that, the report will focus on studying the state of the catalysts using a number of physicochemical tools (XRF, XPS, XANES), including *in situ* investigations. Moreover, the additional use of the synchrotron radiation capabilities makes it possible to clarify the detailed aspects of the structure and chemical state of the elements, beyond the scope of traditional approaches.

**Acknowledgement.** This work was supported by the RF Ministry of Education and Science, agreement no. 14.575.21.0171, identification number RFMEFI57517X0171.

### References:

- [1] A.A. Smirnov, S.A. Khromova, D.Y. Ermakov, O.A. Bulavchenko, A.A. Saraev, P.V. Aleksandrov, V.V. Kaichev, V.A. Yakovlev. *Appl. Catal. A: Gen.* 514 (2016) 224-234.
- [2] I.N. Shilov, A.A. Smirnov, O.A. Bulavchenko, V.A. Yakovlev, *Catalysts* 8 (2018) 560:1-24.
- [3] M.V. Alekseeva (Bykova), D.S. Otyuskaya, M.A. Rekhtina, O.A. Bulavchenko, O.A. Stonkus, V.V. Kaichev, S.G. Zavarukhin, J.W. Thybaut, V. Alexiadis, R.H. Venderbosch, V.A. Yakovlev. *Appl. Catal. A: Gen.* 573 (2019) 1-12.

## Application of Pair Distribution Function Analysis to Structural Studies of Supported Catalysts

Pakharukova V.P.<sup>1,2</sup>

1 – Boreskov Institute of Catalysis, Novosibirsk, Russia

2 – Novosibirsk State University, Novosibirsk, Russia

verapakh@catalysis.ru

The rational design of catalytic materials is related to abilities to effectively probe nano-scale structures. There is significant drawback to common XRD methods addressed to well-crystallized materials, since catalyst components are often highly dispersed and present at low concentrations. The Pair Distribution Function (PDF) analysis based on operating with total scattering data [1-3] is one of the techniques of choice for structural characterization of catalytic materials. Structural characterization of catalysts by the PDF analysis has attracted particular interest in the last years; the method has already proven itself a powerful technique for the study on highly dispersed, defect-rich and amorphous components of catalysts. The PDF,  $G(r)$ , describes local atomic structure of the material and provides structural information in the form of a radial distribution function of inter-atomic distances [1, 4-5]. The relationship between the  $G(r)$  function and the X-ray scattering function is defined through the Fourier transform:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{\infty} Q \cdot S(Q) \cdot \sin(Qr) \cdot dQ, \quad (1)$$

$$G(r) = 4\pi r [\rho(r) - \rho_0], \quad (2)$$

where  $G(r)$  is PDF,  $\rho(r)$  and  $\rho_0$  are the local and average atomic number densities,  $S(Q)$  is the structural part of the scattering intensity,  $Q = (4\pi \sin\theta)/\lambda$  is the magnitude of the wave-vector,  $\lambda$  is the radiation wavelength.

The position of peaks in the PDF correspond directly to interatomic distances within a material; the peak area is related to abundance of the corresponding atomic pair (coordination number). The resolution of the PDF depends significantly on  $Q$  range measured and used in the Fourier transform. Total scattering experiments for the PDF analysis can be done with conventional X-ray diffraction sources (Mo/Ag radiation), but synchrotron facilities provide significantly improved data quality (excellent signal to noise ratio) and quantity (extended  $Q$  range) in substantially reduced measurement times.

In the talk, the PDFs calculated from synchrotron radiation data for different catalysts will be presented and types of structural information extracted from the PDFs will be discussed. The possibilities of the method to probe structure of supported nanoparticles in catalysts will be shown for some examples: 1) mono- and bimetallic (Pt, Rh)/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts for hydrocarbon oxidation; 2)  $\text{MoS}_2/\text{Al}_2\text{O}_3$  hydrotreating catalysts; 3)  $\text{Cu}/\text{ZrO}_2$  catalyst for ethanol steam



## OP-16

reforming. The data will illustrate that the PDF analysis is effective tool for study on structural organization of the supported catalysts and can be used to not only determine the nanoparticle structure but also assess particle shape, size of atomic ordering and possible metal-support interaction.

**Acknowledgement.** This work was supported by Ministry of Science and Higher Education of the Russian Federation (project AAAA-A17-117041710079-8).

The author is grateful to G.A. Bukhtiyarova and L.M. Kovtunova for catalysts provided.

### References:

- [1] E.M. Moroz, V.P. Pakharukova, A.N. Shmakov, Nucl. Instrum. Methods A 603 (2009) 99.
- [2] P.J. Chupas, K.W. Chapman, H. Chen, C.P. Grey, Catal. Today 145 (2009) 213.
- [3] V. Pakharukova, I. Pakharukov, V. Bukhtiyarov, V. Parmon Appl. Catal. A: Gen. 486 (2014) 12-18.
- [4] Egami T. In: Local Structure from Diffraction. Eds. S.J.L. Billinge and M.F. Thorpe. - New York: Plenum, 1998. – P. 1-21.
- [5] *Egami T., Billinge S.J.L.* Underneath the Bragg Peaks: Structural Analysis of Complex Materials. – UK, Oxford: Pergamon Press, 2003.

## Nanoscale Catalytic Systems Based on Alumina and Aluminum Hydroxides. Research Using the PDF Method

Shefer K.I.<sup>1,2</sup>, Moroz E.M.<sup>1</sup>

*1 – Boreskov Institute of Catalysis, Novosibirsk, Russia*

*2 – Novosibirsk State University, Novosibirsk, Russia*

*shefer@catalysis.ru*

The structure of substances is one of the main factors that determines their properties. In the case of catalysts, studying their structure is necessary for understanding the course of catalytic processes and their further goal-oriented synthesis with the required properties. The most reliable structural information is obtained using direct structural diffraction methods. In the case of nanosystems, applying the usual X-ray diffraction methods, which are based on the analysis of the position and intensity of diffraction peaks and which give information about the average atomic and real structure, may be difficult for this investigation. Studying actual nanoscale catalytic systems' structures requires using special diffraction methods based on a complete profile analysis of diffraction patterns, including diffuse scattering. One of these methods is the PDF method. The PDF method allows the establishment of the local structure, present in any system, as well as the phase composition, dispersion, and the possible interaction between the components of a multicomponent system [1, 2]. We get X-ray diffraction patterns for calculating PDF curves at the Siberian Synchrotron and Terahertz Radiation Center (Institute of Nuclear Physics, SB RAS, Novosibirsk). Using a powerful radiation source improves the precision of diffraction experiments and greatly expands the capabilities of the PDF method.

The catalysts' composition may include various oxide systems. Alumina are of great importance for catalysis, and they are used mainly in nanoscale form. At the same time, the structure of such oxides is an interesting and complicated subject for research. When studying oxides, it is important to know the structure of the hydroxides and their precursors. Aluminium hydroxides and aluminas obtained by other methods have different properties and characteristics. This report presents the results of a study of the structural features of such systems using the PDF method.

**Acknowledgement.** This work was carried out within the framework of the budget project #AAAA-A17-117041710079-8 for Boreskov Institute of Catalysis.

### References:

[1] Moroz E.M. X-Ray Diffraction Structure Diagnostics of Nanomaterials // Russian Chemical Reviews. 2011. V.80. N4. P.293-312.

[2] Moroz E.M. X-Ray Structural Characterization of Heterogeneous Catalysts Current Topics in Catalysis. 2016. V.12. P.101-126.

## Photoelectron Diffraction and Holography for Surface Structure Studies

Kuznetsov M.V.<sup>1</sup>, Ogorodnikov I.I.<sup>1</sup>, Usachov D.Yu.<sup>2</sup>, Yashina L.V.<sup>3</sup>

1 – Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences,  
Ekaterinburg, Russia

2 – Saint Petersburg State University, Department of Physics, Saint Petersburg, Russia

3 – Moscow State University, Department of Chemistry, Moscow, Russia

kuznetsov@ihim.uran.ru

X-ray photoelectron holography (XPH) is a relatively new method capable of reconstructing and visualizing in real space the coordination of the atom of interest (emitter) belonging to the surface layer of a crystal using experimentally measured angular distribution of emitted photoelectrons over the whole emission hemisphere. This is possible only if the atomic positions of the nearest neighborhood are similar for all the emitters; however, the emitters can be distributed randomly over similar lattice sites. The latter makes the XPH different from other diffraction techniques such as XRD, LEED, etc. Although the photoelectron diffraction experiment is usually time-consuming, in many cases it brings unique information which is not retrievable using other methods. The experimental data present  $2\pi$  X-ray photoelectron diffraction (XPD) patterns recorded as a photoemission peak intensity at the emitter core level. The XPD patterns are considered as a hologram and can be converted into a real-space image of the atomic structure, thus enabling the direct reconstruction of the local environment around a certain atom. Hence, no assumptions about the structure are required to be made *a priori*.

The depth of analysis for these methods is of the order of several nanometers. The methods are remarkable for their sensitivity to the nature of the examined atoms and to the chemical state of the elements under examination. Further development of the XPD and PEH methods show promise in view of their capabilities to reconstruct 3D images of the atomic structure of the surface layers, to precisely define interatomic distances, and to determine positions of adsorbate atoms on the surface or of impurity atoms inserted into the surface layer structure. That may be of interest, for example, in the experiments modeling the processes run during catalysis. The authors of the report enhance significantly the XPD and PEH capabilities through combining their advantages and refining the surface structure analysis technique. The advanced XPD Processor program is proposed to unify the XPD and PEH in a single approach that allows, in particular, a three-dimensional atomic image of a 2-3 nanometers surface layer to be obtained.

The methods of XPD and PEH can be realized in specialized laboratory spectrometers; however, better results can be achieved with the use of synchrotron sources.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 18-73-00197.

## The Rich Surface Oxygen Chemistry of Perovskites as Revealed by Synchrotron Based Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

Koch G.<sup>1,2</sup>, Hävecker M.<sup>2,3</sup>, Kube P.<sup>2</sup>, Bellini G.<sup>3</sup>, Trunschke A.<sup>3</sup>, Stotz E.<sup>3</sup>, Schlögl R.<sup>2,3</sup>

1 – TU Berlin, BasCat-BASF Joint Lab, Berlin, Germany

2 – MPI for Chemical Energy Conversion, Mülheim a.d.Ruhr, Germany

3 – Fritz Haber Institute, Berlin, Germany

mh@fhi-berlin.mpg.de

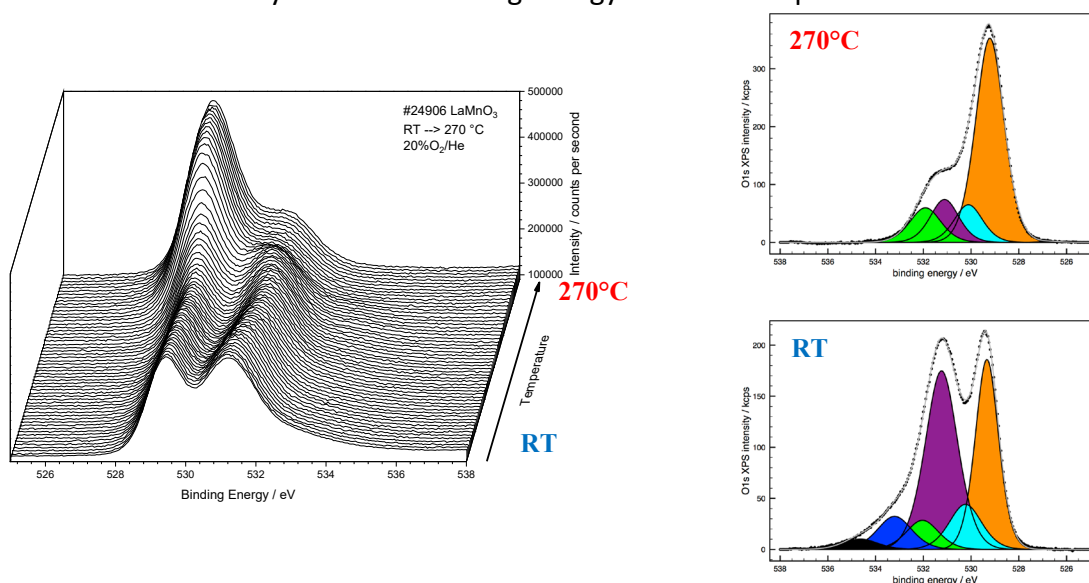
The surface of functional materials like catalysts responds to the ambient conditions. X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS) are one of the most versatile methods for the investigation of surfaces on the atomic scale providing quantitative information about the elemental composition and chemical specificity. Surface sensitive *in situ* spectroscopy, i.e. in the presence of a reactive environment allows studying the formation of the interface (gas/solid or liquid/solid) of a catalyst with time and thus adds a dynamic dimension to the spectroscopic characterization.

Perovskite materials are nowadays discussed in many material science disciplines. Among these are optoelectronics, solar cell and fuel cell applications, and in heterogeneous catalysis [1]. One of the promising characteristics of these materials is that it seems feasible to address and tune many properties for the desired application due to the various compositions of pure and partially substituted  $AA'A''BB'B''(O,X)_3$  perovskites [2]. In heterogeneous catalysis perovskite are known as combustion catalysts but these materials are also candidates for low temperature selective propane oxidative dehydrogenation, for instance. As a promising way to achieve meaningful selectivity in propane dehydrogenation to propene Mn-based perovskites with exposed  $MnO_x$  species on the surface have been suggested.

Hence, we have synthesized several  $La(Sm)MnO_3$  perovskites with different La/Mn and Sm/Mn ratio, respectively, featuring a different amount of  $MnO_x$  species on the surface. These bulk materials have been studied under various conditions including oxygen, and dry and wet propane oxidative dehydrogenation feed with surface sensitive ambient pressure XPS (AP-XPS) and soft-XAS. Beside the surface atom ratio of for instance La and Mn, the oxygen surface structure has been studied in detail. The oxygen surface chemistry of perovskites is very rich with not only adsorbed oxygen species present beside the lattice oxygen but also defect oxygen sites can be created to balance the excess or deficiency of La.

Figure 1 shows the evolution of O1s XPS spectra of a  $LaMnO_3$  catalyst heated from room temperature to the reaction temperature of 270°C. Differently coordinated oxygen unveils by a different binding energy. A constrained fit of all spectra obtained during the heating ramp with 5K/min suggest the presence of various oxygen species. The assignment of fitted components to adsorbed oxygen species, defect oxygen, and matrix oxygen will be discussed.

Although the surface of perovskites has been studied by XPS in detail in the literature [3], there is still some controversy about the binding energy of different species.



**Figure 1:** The left panel depicts the evolution of O1s XPS spectra during the heating of LaMnO<sub>3</sub> from room temperature to 270°C in a 5%O<sub>2</sub>/He mixture, total pressure is 25Pa. A constrained deconvolution of each spectrum suggest the presence of at least 6 different oxygen species. The single spectra on the right panels exemplify the fit of the O1s spectra at room temperature and the final temperature of 270°C, respectively.

In summary, we present Mn-based catalyst for low temperature oxidative dehydrogenation of propane free of vanadium. The abundance of MnO<sub>x</sub> species on the surface correlates with the increase in selectivity to propene. We observe the formation of hydroxyls, defects, and carbonates on the surface. Considering a huge data set from employing AP-XPS is a key to disentangle the various oxygen species and their evolution during reaction conditions.

Finally, the status of and an outlook on some of the current and future instrumentation and activities of the Fritz Haber Institute at HZB/BESSY to develop further synchrotron based ambient pressure characterization methodologies will be given. The *ISIS* facility (Innovative Station for In-situ Spectroscopy) is in user operation since 2007, while *BEIC*Chem, the Berlin Electrochemistry Laboratory) has recently been put into operation. The *CAT@EMIL* (Energy Materials In-situ Laboratory Berlin) laboratory is under commissioning. All facilities are equipped with state of the art AP-XPS spectrometer. Status, similarities and differences of these three facilities based at HZB/BESSY will be discussed.

**Acknowledgement.** St. Lohr is acknowledged for continuous support during synthesis. Synchrotron beamtime has been provided by HZB/BESSY under proposal number 17205966.

#### References:

- [1] P.G. Szuromi, B. Grocholski, *Science* 10 (2017) 732.
- [2] D. Royer et al., *Chem. Rev.* 114 (2014) 10292.
- [3] K.A. Stoerzinger et al., *J. Phys. Chem. C* 118 (2014) 19733.

## In Situ/Ex Situ Study of Model Rh-Doped CeO<sub>2</sub> Catalysts

Kibis L.S.<sup>1,2</sup>, Svintsitskiy D.A.<sup>1,2</sup>, Derevyannikova E.A.<sup>1</sup>, Kardash T.Yu.<sup>1,2</sup>, Slavinskaya E.M.<sup>1,2</sup>,  
Stonkus O.A.<sup>1,2</sup>, Svetlichnyi V.A.<sup>3</sup>, Boronin A.I.<sup>1,2</sup>

1 – Boreskov Institute of Catalysis, Novosibirsk, Russia

2 – Novosibirsk State University, Novosibirsk, Russia

3 – Tomsk State University, Tomsk, Russia

kibis@catalysis.ru

Despite its high price, Rh remains an indispensable component of the current catalytic converters of automobile exhausts. The Rh-doped CeO<sub>2</sub> catalysts comprising Rh<sup>3+</sup> species ionically dispersed in the CeO<sub>2</sub> lattice can be considered as potential catalysts which provide the maximum catalytic efficiency of the expensive active component. These catalysts proved to be active in low-temperature CO oxidation and NO reduction [1,2]. However, the nature of the active species and their stability still need to be clarified.

In this work, the thermal stability and redox properties the Rh-doped CeO<sub>2</sub> catalysts were studied by a combination of structural (XRD, TEM) and spectroscopic (FT-IR, XPS, Raman) methods. Samples were prepared by co-precipitation of rhodium and cerium nitrates (Rh(NO<sub>3</sub>)<sub>3</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>).

Rh<sup>3+</sup> species incorporated in the CeO<sub>2</sub> lattice are stable up to 800°C. Calcination of the samples above this temperature results in segregation of Rh<sup>3+</sup> ions out of CeO<sub>2</sub> lattice with the formation of Rh<sub>2</sub>O<sub>3</sub> oxides on the CeO<sub>2</sub> surface. The redox properties of the catalysts calcined at different temperatures were studied by *in situ* XRD and FT-IR methods as well as *ex situ* XPS. According to *in situ* XRD data the structural changes of Rh<sup>3+</sup>-CeO<sub>2</sub> catalysts are observed upon interaction with CO at T>100°C. The formation of the finely dispersed metal Rh<sub>n</sub><sup>0</sup> particles can be detected after CO exposure at 400°C. Reoxidation with O<sub>2</sub> leads to the reverse interaction of Rh<sub>n</sub><sup>0</sup> particles with the CeO<sub>2</sub> surface. *In situ* FT-IR data show the reduction of dispersed Rh<sup>3+</sup> species upon interaction with CO already at 50°C while the reduction of Rh<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub> samples requires a higher temperature. *Ex situ* XPS experiments reveal a substantial reduction of Ce<sup>4+</sup> species upon treatment of Rh<sup>3+</sup>-CeO<sub>2</sub> samples with CO. Both Rh<sub>n</sub><sup>0</sup> and Ce<sup>3+</sup> species are easily reoxidized by O<sub>2</sub> even at room temperature.

It can be concluded that a high degree of metal-support interaction in Rh<sup>3+</sup>-CeO<sub>2</sub> catalysts provides the efficient reversible transitions Rh<sup>3+</sup> ↔ Rh<sub>n</sub><sup>0</sup> and Ce<sup>4+</sup> ↔ Ce<sup>3+</sup> facilitating the catalytic reactions in a low-temperature range.

**Acknowledgement.** This work was partially supported by the Russian Foundation for Basic Research and the government of the Novosibirsk region of the Russian Federation, grant №18-43-543009.

### References:

- [1] A. Gayen et al. Chem. Mater. 16 (2004) 2317.  
[2] S. Roy et al. Appl. Energy 86 (2009) 2283.

## Spectroscopic Insights to Rh-Ga Alloys as Model Systems for a Novel Type of Dehydrogenation Catalyst

Wittkämper H.<sup>1</sup>, Raman N.<sup>2</sup>, Grabau M.<sup>1</sup>, Maisel S.<sup>3</sup>, Taccardi N.<sup>2</sup>, Debuschewitz J.<sup>2</sup>, Bauer T.<sup>5</sup>, Wu M.<sup>4</sup>, Haumann M.<sup>2</sup>, Görling A.<sup>3</sup>, Spiecker E.<sup>4</sup>, Libuda J.<sup>5</sup>, Wasserscheid P.<sup>2</sup>, Steinrück H.-P.<sup>1</sup>, Papp C.<sup>1</sup>

1 – Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Physikalische Chemie II, Erlangen, Germany

2 – Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Chemische Reaktionstechnik (CRT), Erlangen, Germany (pt 12)

3 – Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Theoretische Chemie, Erlangen, Germany

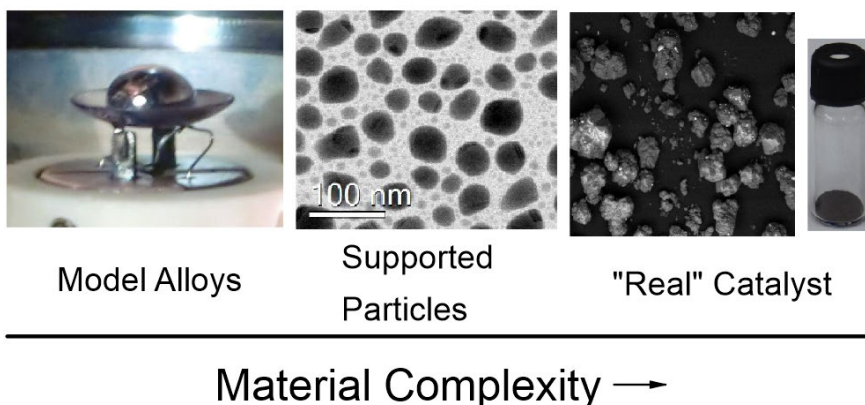
4 – Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Werkstoffwissenschaften, Mikro- und Nanostrukturforschung, Erlangen, Germany

5 – Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Katalytische Grenzflächenforschung, Erlangen, Germany

haiko.wittkaemper@fau.de

We present a study of Rhodium as active metal for selective alkane dehydrogenation. It becomes a very active, selective and stable propane dehydrogenation catalyst when incorporated in a matrix of liquid gallium on oxidic support particles. This catalytic concept was pioneered by some of us and is termed *SCALMS*, which is the acronym for *supported catalytically active liquid metal solutions*. We have a general interest in the surface/interfacial properties of this novel type of catalysts and have previously reported findings for similar systems based on PtGa and PdGa alloys.[1-4]. The remarkable properties of the catalysts are attested to the atomic dispersion of the active transition metal in liquid gallium nano-droplets, and the dynamics at the liquid metal/gas interface. For the Rhodium-based catalyst, we present temperature-dependent photoelectron spectroscopy studies of macroscopic model alloy systems, particles systems prepared by physical vapor deposition, and real catalyst samples (Figure 1). Our findings link temperature-dependent changes in the reactivity of the catalyst to the dissolution/precipitation of Rh-rich intermetallic phases, leading to the Rh enrichment/depletion of the liquid Ga phase. Besides that, we investigated changes in the surface composition of RhGa alloys during oxidation for both macroscopic alloy droplets and nanoparticles utilizing lab-based and synchrotron-based XPS. Furthermore, high resolution temperature-dependent transmission electron microscopy studies of the RhGa particle systems are presented. Based on *ab initio* molecular dynamics simulations and density functional theory calculations of a possible reaction site, a mechanism for the system is proposed, which is in line with our findings.





**Figure 1:** Material complexity in the context of the studied RhGa SCALMS system: To illuminate the underlying working principles of the technically applied catalyst, the knowledge gained from a simple model alloy is transferred to progressively more complex material systems.

#### References:

- [1] M. Grabau, J. Erhard, N. Taccardi et al., *Spectroscopic Observation and Molecular Dynamics Simulation of Ga Surface Segregation in Liquid Pd–Ga Alloys.*, *Chem. Eur. J.*, (2017).
- [2] N. Taccardi, M. Grabau, J. Erhard et al., *Gallium-rich Pd-Ga phases as supported liquid metal catalysts*, *Nat. Chem.* 9, 862-867 (2017).
- [3] M. Grabau, S. K. Calderon, F. Rietzler et al., *Surface enrichment of Pt in Ga<sub>2</sub>O<sub>3</sub> films grown on liquid Pt/Ga alloys*, *Surf. Sci.* **651**, 16-21 (2016).
- [4] N. Raman, S. Maisel, M. Grabau, et al., *Highly Effective Propane Dehydrogenation Using Ga-Rh Supported Catalytically Active Liquid Metal Solutions*, submitted.



## ***In Situ* Study of Dehydrogenation of Propane over Vanadia-Titania Catalysts**

Kaichev V.V.<sup>1,2</sup>, Chesalov Yu.A.<sup>1,2</sup>, Saraev A.A.<sup>1,2</sup>, Tsapina A.M.<sup>1</sup>

1 – Borekov Institute of Catalysis, Novosibirsk, Russia

2 – Novosibirsk State University, Novosibirsk, Russia

vvk@catalysis.ru

The oxidative and non-oxidative dehydrogenation of propane over a monolayer  $V_2O_5/TiO_2$  catalyst was examined using *in situ* Fourier-transform infrared spectroscopy (FTIR) and *pseudo in situ* X-ray photoelectron spectroscopy (XPS). According to FTIR, the catalyst surface contains isopropoxide, acetone, formate, acetate, and carbonate species in both cases. The fresh calcined catalyst contains vanadium in the  $V^{5+}$  state; however, its treatment in the propane flow leads to the reduction of  $V^{5+}$  to  $V^{3+}$ . Simultaneously, the catalyst treatment in propane leads to the formation of Ti–O–H groups, the removal of vanadyl oxygen species, and accumulation of carbonaceous deposits. Besides, XPS data indicate that the reduction of catalyst is accompanied by reversible destruction of the vanadia monolayer and formation of 3D clusters or nanoparticles on the titania surface, which leads to catalyst deactivation. In contrast, under the action of a propane/oxygen mixture flow, the accumulation of carbonaceous deposits and the destruction of the vanadia monolayer do not proceed;  $V^{5+}$  cations are partially reduced to  $V^{4+}$ . We suggest that the oxidative dehydrogenation of propane to propylene over vanadium oxide-based catalysts proceeds via the redox mechanism, where the oxidized catalyst surface oxidizes propane and is reoxidized by gas-phase oxygen. The active sites contain  $V^{5+}$  cations, and the C–H bond of propane is activated mainly on the vanadyl oxygen species. The key intermediate is isopropoxide, which can transform to propylene or acetone. Adsorbed acetone is unstable and is oxidized further to formate and acetate species, which could be oxidized to CO and  $CO_2$ . In contrast, the non-oxidative dehydrogenation of propane proceeds over the reduced catalyst. In this case, active sites contain coordinatively unsaturated  $V^{3+}$  cations. The mechanisms of both reactions are discussed.

Computer Modeling of CdS-TiO<sub>2</sub> Heterojunctions in Photo Catalyst

Balyakin I.A.<sup>1,2,3</sup>, Rempel A.A.<sup>1,2,3</sup>

1 – Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia

2 – Ural Federal University, Ekaterinburg, Russia

3 – Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia  
i.a.balyakin@gmail.com

CdS/TiO<sub>2</sub> heterostructures are widely studied in photocatalysis [1]. Understanding the photocatalytic mechanism is necessary for designing of new effective photocatalysts. Band line-up in heterojunctions is directly connected with charge transfer, which is in turn determines photocatalytic mechanism. Band line-up for heterojunctions may be calculated via density functional theory (DFT) [2].

In this work the band line-up calculation for CdS/TiO<sub>2</sub> heterjunction via CP2K [3] code was performed. First, both semiconductors were treated separately: TiO<sub>2</sub> (anatase) demonstrated Valence Band Maximum (VBM) at 5.09 eV, CdS (greenokit) demonstrated VBM at 2.63 eV. After that CdS/TiO<sub>2</sub> heterojunction was treated by CP2K in order to obtain electrostatic potential distribution *V* in this system. Valence band offset (VBO) for CdS/TiO<sub>2</sub> heterojunction was calculated as follows

$$VBO = \Delta V_{BM} + e\Delta V, \tag{1}$$

where *e* is the charge of the electron,  $\Delta V$  is the difference between mean values of electrostatic potential in TiO<sub>2</sub> and CdS, according to our calculation  $e\Delta V=3.44$  eV (electrostatic energy in CdS is higher). Conduction Band Offset (CDO) was calculated from VBO and empirical data for band gap width in both semiconductors. DFT data was not used in CDO determination since DFT is not able to accurately predict band gap width.

Predicted band line-up for TiO<sub>2</sub>/CdS heterojunction is represented in the figure.

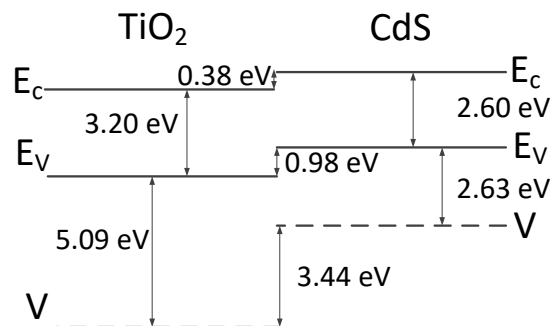


Figure. Band line-up for TiO<sub>2</sub>/CdS heterojunction

## OP-23

**Acknowledgement.** This work was financially supported by the Russian Foundation of Basic Research RFBR No. 17-03-00702.

### References:

1. W. Li *et al*, *Nanomaterials*, 8 (2018) 415.
2. C. Van de Walle, *Phys. Rev. B*, 34 (1986) 34.
3. J. Hutter *et al*, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 4 (2014) 15.

## List of Participants

**ABDEL-MAGEED A.M.**

Ulm University, Institute of Surface Chemistry  
and Catalysis  
Ulm, Germany  
[ali.abdel-mageed@uni-ulm.de](mailto:ali.abdel-mageed@uni-ulm.de)

**ALEKSEEVA Mariya**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[bykova@catalysis.ru](mailto:bykova@catalysis.ru)

**ALIKIN Evgeny**

Ecoalliance LTD  
Novouralsk, Russia  
[alikin@eco-nu.ru](mailto:alikin@eco-nu.ru)

**BAKSHEEV Evgeny**

Ecoalliance LTD  
Novouralsk, Russia

**BALYAKIN Ilya**

Institute of Metallurgy of the Ural Branch  
of the RAS  
Ekaterinburg, Russia  
[i.a.balyakin@gmail.com](mailto:i.a.balyakin@gmail.com)

**BEHM R. Jürgen**

Ulm University,  
Institute of Surface Chemistry and Catalysis  
Ulm, Germany  
[Juergen.behm@uni-ulm.de](mailto:Juergen.behm@uni-ulm.de)

**BELYAKOVA Olga**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[olbelyak@gmail.com](mailto:olbelyak@gmail.com)

**BUKHTIYAROV Andrei**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[avb@catalysis.ru](mailto:avb@catalysis.ru)

**BUKHTIYAROV Valerii**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[vib@catalysis.ru](mailto:vib@catalysis.ru)

**BUKHTIYAROVA Marina**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[mvb@catalysis.ru](mailto:mvb@catalysis.ru)

**BULAVCHENKO Olga**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[isizy@mail.ru](mailto:isizy@mail.ru)

**HÄVECKER Michael**

MPI for Chemical Energy Conversion  
Berlin, Germany  
[mh@fhi-berlin.mpg.de](mailto:mh@fhi-berlin.mpg.de)

**KAICHEV Vasily**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[vvk@catalysis.ru](mailto:vvk@catalysis.ru)

**KIBIS Lidiya**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[kibis@catalysis.ru](mailto:kibis@catalysis.ru)

**KISKINOVA Maya**

Elettra Sincrotrone Trieste  
Trieste, Italy  
[maya.kiskinova@elettra.eu](mailto:maya.kiskinova@elettra.eu)

**KNOP-GERICKE Axel**

MPI of Chemical Energy Conversion  
Mülheim, Germany  
[knop@fhi-berlin.mpg.de](mailto:knop@fhi-berlin.mpg.de)

**KUZNETSOV Mikhail**

Institute of Solid State Chemistry of UB RAS  
Ekaterinburg, Russia  
[kuznetsov@ihim.uran.ru](mailto:kuznetsov@ihim.uran.ru)

**LOGUNOVA Svetlana**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[logunova@catalysis.ru](mailto:logunova@catalysis.ru)

**MAMATKULOV Mikhail**

Boreskov Institute of Catalysis  
Novosibirsk, Russia  
[mikhail@catalysis.ru](mailto:mikhail@catalysis.ru)

**NIKITINA Nadezhda**

Lomonosov Moscow State University  
Moscow, Russia  
[nnikitina1719@gmail.com](mailto:nnikitina1719@gmail.com)

## List of Participants

**PAKHARUKOVA Vera**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[verapakh@catalysis.ru](mailto:verapakh@catalysis.ru)

**SARAEV Andrey**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[asaraev@catalysis.ru](mailto:asaraev@catalysis.ru)

**SAVINOVA Elena**

ICPEES  
Strasbourg, France  
[elena.savinova@unistra.fr](mailto:elena.savinova@unistra.fr)

**SCHLÖGL Robert**

Fritz-Haber Institute on the Max Planck  
Society  
Berlin, Germany  
[acsek@fhi-berlin.mpg.de](mailto:acsek@fhi-berlin.mpg.de)

**SELIVANOVA Aleksandra**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[avselivanova@catalysis.ru](mailto:avselivanova@catalysis.ru)

**SHEFER Kristina**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[shefer@catalysis.ru](mailto:shefer@catalysis.ru)

**SHMAKOV Alexander**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[shurka@catalysis.ru](mailto:shurka@catalysis.ru)

**SKORUPSKA Katarzyna**

Fritz-Haber-Institut der Max-Planck-  
Gesellschaft  
Berlin, Germany  
[skorupska@fhi-berlin.mpg.de](mailto:skorupska@fhi-berlin.mpg.de)

**SMIRNOVA Nadezhda**

N.S. Kurnakov Institute of General and  
Inorganic Chemistry RAS  
Moscow, Russia  
[felisine@gmail.com](mailto:felisine@gmail.com)

**STEINRÜCK Hans-Peter**

Friedrich-Alexander-Universität  
Erlangen-Nürnberg  
Erlangen, Germany

**STOTZ Eugen**

Fritz-Haber Institute on the Max Planck  
Society  
Berlin, Germany  
[stotz@fhi-berlin.mpg.de](mailto:stotz@fhi-berlin.mpg.de)

**SULZMANN Frederic Paul**

Fritz-Haber Institute on the Max Planck  
Society  
Berlin, Germany  
[frederic@fhi-berlin.mpg.de](mailto:frederic@fhi-berlin.mpg.de)

**SUVOROVA Marina**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[ms-suvorova@yandex.ru](mailto:ms-suvorova@yandex.ru)

**TSAPINA Anna**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[amtsapina@catalysis.ru](mailto:amtsapina@catalysis.ru)

**van de KROL Roel**

Institute for Solar Fuels  
Berlin, Germany

**WITTKÄMPER Haiko**

Friedrich-Alexander-Universität Erlangen-  
Nürnberg  
Erlangen, Germany  
[Haiko.wittkaemper@fau.de](mailto:Haiko.wittkaemper@fau.de)

**ZUBAVICHUS Yan**

Boreshkov Institute of Catalysis  
Novosibirsk, Russia  
[yzubav@gmail.com](mailto:yzubav@gmail.com)

## Content

<b>Plenary Lectures</b> .....	<b>5</b>
<b>PL-1</b> Knop-Gericke A. <b>The Electronic Structure of Solid/Liquid Interfaces Relevant for Water Oxidation and Carbondioxide Reduction</b> .....	<b>7</b>
<b>PL-2</b> Zubavichus Y.V. <b>Structural Diagnostics of Catalysts Using X-Ray Synchrotron Radiation: Current Possibilities and Future Prospects</b> .....	<b>8</b>
<b>PL-3</b> Savinova E.R. <b>Electrocatalysis at the Molecular Level: from Electrochemical Methods to In Situ Spectroscopies</b> .....	<b>9</b>
<b>PL-4</b> Steinrück H.-P. <b>Surface Science of Low Vapor Pressure Liquids</b> .....	<b>10</b>
<b>PL-5</b> Van de Krol R., Friedrich D., Eichberger R., Favaro M., Starr D.E. <b>Time-Resolved and Operando Photoemission Studies on Metal Oxide Photoelectrodes</b> .....	<b>11</b>
<b>PL-6</b> Kiskinova M. <b>Microscopic Insights on Properties of Catalysts Using Synchrotron-Based Methods</b> .....	<b>13</b>
<b>Oral Presentations</b> .....	<b>15</b>
<b>OP-1</b> Shmakov A.N., Vinokurov Z.S., Yakushkin S.S., Nesterov N.S., Martyanov O.N. <b>High Energy X-Ray Synchrotron In Situ and Operando Diagnostics of Heterogeneous Catalysts</b> .....	<b>17</b>
<b>OP-2</b> Belyakova O.A., Zubavichus Ya.V., Vasil'kov A.Y., Naumkin A.V. <b>The Study of Au/Ni Bimetallic Nanoparticles Using a Combination of XAFS, XRD and SAXS/ASAXS Synchrotron Techniques</b> .....	<b>18</b>
<b>OP-3</b> Pichugina D.A., Nikitina N.A., Kuz'menko N.E. <b>On the Mechanism of CO Oxidation on Gold Nanocluster: Ligand and Doping Effects</b> .....	<b>19</b>

<b>OP-4</b>	
<u>Bukhtiyarov A.V.</u> , Prosvirin I.P., Mamatkulov M., Yudanov I.V., Klyushin A.Yu., Knop-Gericke A., Neyman K.M., Bukhtiyarov V.I.	
<b>CO Oxidation on the Model Pd-Au/HOPG Catalysts: NAP XPS and MS Study</b> .....	<b>20</b>
<b>OP-5</b>	
<u>Mamatkulov M.I.</u> , Yudanov I.V., Neyman K.M.	
<b>Atomic Ordering in Bimetallic Pd-Au Nanoparticles: Computational Study of Pd Surface Segregation in Reactive Environment</b> .....	<b>22</b>
<b>OP-6</b>	
Wiese K., Rezvani A., Abdel-Mageed A.M., Klyushin A., Knop-Gericke A., Schlögl R., <u>Behm R.J.</u>	
<b>Insights into Fundamental Aspects of Au Catalysis from Operando and In Situ Spectroscopy: Methanol Synthesis on Au/ZnO as a Key Example</b> .....	<b>24</b>
<b>OP-7</b>	
<u>Smirnova N.S.</u> , Khramov E.V., Stolyarov I.P., Cherkashina N.V., Baeva G.N., Bragina G.O., Yakushev I.A., Mashkovsky I.S., Vargaftik M.N., Stakheev A.Yu.	
<b>The Investigation of Thermal Decomposition of Heterobimetallic PtZn(CH<sub>3</sub>COO)<sub>4</sub> Acetate Complex in Reductive Conditions by <i>In Situ</i> XAFS</b> .....	<b>26</b>
<b>OP-8</b>	
<u>Abdel-Mageed A.M.</u> , Fauth C., Rungtaweeworanit B., Yaghi O.M., Behm R.J.	
<b>On the Electronic and Geometric Structure of a Single Atom Cu/UiO-66 Catalyst during CO Oxidation: An Operando FTIR and XAFS Study</b> .....	<b>28</b>
<b>OP-9</b>	
<u>Saraev A.A.</u> , Tsapina A.M., Selivanova A.V., Fedorov A.V., Vorokhta M., Šmíd B., Kaichev V.V.	
<b>NAP XPS Study of CO Oxidation over CuFeAl Nanocomposite Catalysts</b> .....	<b>30</b>
<b>OP-10</b>	
<u>Bulavchenko O.A.</u> , Vinokurov Z.S., Afonassenko T.N. , Tsyryl'nikov P.G., Saraev A.A., Kaichev V.V., Tsybulya S.V.	
<b>In Situ XRD and XPS Study of the Reduction Process of Mixed Mn-Zr Oxide Catalysts of CO Oxidation</b> .....	<b>31</b>
<b>OP-11</b>	
<u>Skorupska K.</u> , Jone D.T., Mom R., Sulzmann F., Chuang Ch.-H., Melder J., Kurz P., Knop-Gericke A., Schlögl R.	
<b>Manganese Oxides under OER</b> .....	<b>33</b>
<b>OP-12</b>	
<u>Stotz E.</u> , Hävecker M., Valsco-Velez J.J., Knop-Gericke A., Schlögl, R.	
<b>Modular Concept for Catalysis Research at BESSY from an Engineer Point of View</b> .....	<b>34</b>
<b>OP-13</b>	
<u>Sulzmann F.</u> , Carbonio E., Jones T., Knop-Gerincke A., Schlögl R.	
<b>Differentiation of Strongly Bound Oxygen on Silver</b> .....	<b>35</b>

<b>OP-14</b>	
<u>Bukhtiyarova M.V.</u> , Prosvirin I.P., Bukhtiyarov A.V., Panafidin M.A.	
<b>In Situ XPS Study of Selective Methanol Oxidation over Cu Catalysts on the Base of Layered Double Hydroxides .....</b>	<b>37</b>
<b>OP-15</b>	
<u>Alekseeva M.V.</u> , Smirnov A.A., Selischeva S.A., Shilov I.N., Fedorov A.V., Bulavchenko O.A., Saraev A.A., Yakovlev V.A.	
<b>In Situ and Advanced Synchrotron Studies of Catalysts for Bio-Oxygenates Hydroconversion .....</b>	<b>38</b>
<b>OP-16</b>	
<u>Pakharukova V.P.</u>	
<b>Application of Pair Distribution Function Analysis to Structural Studies of Supported Catalysts .....</b>	<b>39</b>
<b>OP-17</b>	
<u>Shefer K.I.</u> , Moroz E.M.	
<b>Nanoscale Catalytic Systems Based on Alumina and Aluminum Hydroxides. Reserch Using the PDF Method.....</b>	<b>41</b>
<b>OP-18</b>	
<u>Kuznetsov M.V.</u> , Ogorodnikov I.I., Usachov D.Yu., Yashina L.V.	
<b>Photoelectron Diffraction and Holography for Surface Structure Studies .....</b>	<b>42</b>
<b>OP-19</b>	
<u>Koch G.</u> , <u>Hävecker M.</u> , Kube P., Bellini G., Trunschke A., Stotz E., Schlögl R.	
<b>The Rich Surface Oxygen Chemistry of Perovskites as Revealed by Synchrotron Based Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS).....</b>	<b>43</b>
<b>OP-20</b>	
<u>Kibis L.S.</u> , Svintsitskiy D.A., Derevyannikova E.A., Kardash T.Yu., Slavinskaya E.M., Stonkus O.A., Svetlichnyi V.A., Boronin A.I.	
<b>In Situ/Ex Situ Study of Model Rh-Doped CeO<sub>2</sub> Catalysts .....</b>	<b>45</b>
<b>OP-21</b>	
<u>Wittkämper H.</u> , Raman N., Grabau M., Maisel S., Taccardi N., Debuschewitz J., Bauer T., Wu M., Haumann M., Görling A., Spiecker E., Libuda J., Wasserscheid P., Steinrück H.-P., Papp C.	
<b>Spectroscopic Insights to Rh-Ga Alloys as Model Systems for a Novel Type of Dehydrogenation Catalyst.....</b>	<b>46</b>
<b>OP-22</b>	
<u>Kaichev V.V.</u> , Chesalov Yu.A., Saraev A.A., Tsapina A.M.	
<b>In Situ Study of Dehydrogenation of Propane over Vanadia-Titania Catalysts.....</b>	<b>48</b>
<b>OP-23</b>	
<u>Balyakin I.A.</u> , Rempel A.A.	
<b>Computer Modeling of CdS-TiO<sub>2</sub> Heterojunctions in Photo Catalyst.....</b>	<b>49</b>
<b>List of Participants .....</b>	<b>51</b>
<b>Content.....</b>	<b>53</b>



## Scientific edition

5th Russian-German Seminar  
“Bridging the Gap between Model and Real Catalysis”. Synchrotron Radiation in Catalysis  
June 23-26, 2019 Novosibirsk, Russia

Abstracts

Editors: Prof. Valerii I. Bukhtiyarov, Dr. Marina V. Bukhtiyarova

Compiled by: Marina V. Bukhtiyarova, Marina S. Suvorova  
Computer processing of text: Yulia V. Klimova, Aleksey A. Spiridonov

## Научное издание

V Российско-Немецкий семинар  
«Связь между модельным и реальным катализом». Синхротронные исследования в  
катализе

23-26 июня 2019 года, Новосибирск, Россия

Сборник тезисов докладов

Под общей редакцией: академика В.И. Бухтиярова, к.х.н. М.В. Бухтияровой

Составители: М.В. Бухтиярова, М.С. Суворова

Компьютерная обработка: Ю.В. Климова, А.А. Спиридонов

### Издатель:

**Федеральное государственное бюджетное учреждение науки**  
«Федеральный исследовательский центр «Институт катализа им. Г.К. Борескова  
Сибирского отделения Российской академии наук»  
630090, Новосибирск, пр-т Академика Лаврентьева, 5, ИК СО РАН  
<http://catalysis.ru> E-mail: [bic@catalysis.ru](mailto:bic@catalysis.ru) Тел.: +7 383 330-67-71

### Электронная версия:

Издательский отдел Института катализа СО РАН

E-mail: [pub@catalysis.ru](mailto:pub@catalysis.ru) Тел.: +7 383 326-97-15

Объем: 5 МБ. Подписано к размещению: 17.06.2019

Адрес размещения:

[http://catalysis.ru/resources/institute/Publishing/Report/2019/ABSTRACTS\\_RGS\\_on\\_Catalysis2019.pdf](http://catalysis.ru/resources/institute/Publishing/Report/2019/ABSTRACTS_RGS_on_Catalysis2019.pdf)

Системные требования: i486; Adobe Reader (чтение формата PDF)

ISBN 978-5-906376-23-7





[http://catalysis.ru/resources/institute/Publishing/Report/2019/ABSTRACTS\\_RGS\\_on\\_Catalysis2019.pdf](http://catalysis.ru/resources/institute/Publishing/Report/2019/ABSTRACTS_RGS_on_Catalysis2019.pdf)