



UK Russia seminar on CATALYSIS

AGENDA

20-21 November 2017

Zelinsky Institute of Organic Chemistry

Moscow, Russia

November 20, Monday

Venue: Library, Zelinsky Institute of Organic Chemistry RAS, Leninsky pr., 47, Moscow, Russia

09:00 – 09:30 Arrival, registration and presentations upload

09:30 – 10:00 Welcome remarks

Welcome remarks from Zelinsky Institute - Professor M. P. Egorov, Director

Welcome remarks from the British Embassy – Gareth Wynn Owen, Head Science and Innovation

Welcome remarks from the Royal Society – Professor Richard Catlow

Welcome remarks from seminar co-Chairs Professor Graham Hutchings, Professor Mikhail Egorov, and Professor Valentine Ananikov

Session Chair: Mikhail P. Egorov

10:00 – 10:30 Lecture 1, Professor Graham J. Hutchings (Cardiff University, UK) *Catalysis using gold-containing nanoparticles*

10:30 – 11:00 Lecture 2, Professor Valentine P. Ananikov (Zelinsky Institute, Moscow) *Understanding Active Species in Catalytic Transformations: from Molecular Catalysis to Metal Clusters and Dynamic Nanoparticle Systems.*

11:00 – 11:30 Lecture 3, Professor Richard Catlow (University College London and Cardiff University, UK). *Modelling, neutron scattering and synchrotron radiation studies of structure, dynamics and reactivity in catalytic systems.*

11:30 – 12:00 Lecture 4, Professor Valerii I. Bukhtiyarov (Boreskov Institute of Catalysis, Novosibirsk, Russia). *Active centers in heterogeneous catalysts: formation and study with in situ methods.*

12:00 – 12:15 Group Photo. Gathering in the hall at the Library.

12:15 – 13:30 Lunch

Session Chair: Graham. J. Hutchings

13:30 – 14:00 Lecture 5, Professor Andrea E. Russell (University of Southampton, UK). *In situ X-ray studies of PEM fuel cell electrocatalysts: Bimetallic catalysts for CO tolerance and DAFCs.*

14:00 – 14:30 Lecture 6, Professor Dmitry G. Yakhvarov (Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia). *Electrochemical reactions of transition metal complexes as a way to new catalysts and materials.*

14:30 – 15:00 Lecture 7, Professor Russell Francis Howe (University of Aberdeen, UK). *Operando Infrared Spectroscopy on Zeolite Catalysts Using Synchrotron Radiation.*

15:00 – 15:30 Coffee break

Session Chair: Valentine P. Ananikov

15:30 – 16:00 Lecture 8, Professor Anton L. Maximov (Topchiev Institute of Petrochemical Synthesis, Moscow, Russia). *Slurry-phase hydroprocessing using ultra-dispersed catalysts.*

16:00 – 16:30 Lecture 9, Dr. Andrew Logsdail (Cardiff University, UK). *A computational materials perspective on heterogeneous catalysis.*

16:30 – 17:00 Lecture 10, Professor Victor M. Chernyshev (Platov South-Russian State Polytechnic University, Novocherkassk, Russia). *Conversion of carbohydrates to 5-hydroxymethylfurfural and furan-derived monomers for new generation of polymers and functional materials.*

17:00 – 18:00 Round table discussion

18:30 Dinner

November 21, Tuesday

Venue: Library, Zelinsky Institute of Organic Chemistry RAS, Leninsky pr., 47, Moscow, Russia

09:00 – 09:30 Arrival and presentations upload

Session Chair: Professor Richard Catlow

09:30 – 10:00 Lecture 11, Dr. Jennifer Edwards (Cardiff University, UK). *Novel catalysts for H₂O₂ synthesis and their utilisation in wastewater treatment.*

10:00 – 10:30 Lecture 12, Dr. Elena A. Redina (Zelinsky Institute of Organic Chemistry, Moscow, Russia). *Pt-nanocatalysts for selective room-temperature transformations of carbonyl- and nitro-compounds in the presence of H₂.*

10:30 – 11:00 Lecture 13, Dr. Emma Gibson (University of Glasgow, UK). *Developments in advanced in situ and operando spectroscopy for catalysis.*

11:00 – 11:30 Lecture 14, Dr. Laura Torrente Murciano (University of Cambridge, UK). *Manufacturing of designed heterogeneous catalysts.*

11:30 – 12:30 Lunch

Session Chair: Valerii I. Bukhtiyarov

12:30 – 13:00 Lecture 15, Professor Yulia G. Gorbunova (Kurnakov Institute of General and Inorganic Chemistry, Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia). *Molecular switches based on tetrapyrrolic compounds.*

13:00 – 13:30 Lecture 16, Professor Duncan Wass (University of Bristol, UK). *Homogeneous Catalysts for Advanced Biofuels.*

13:30 – 14:00 Lecture 17, Professor Sergey N. Osipov (Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia). *New Fluorinated Unsymmetrical NHC-Ligands for Metal Catalysis.*

14:00 – 14:30 Lecture 18, Professor Sergey G. Zlotin (Zelinsky Institute of Organic Chemistry, Moscow, Russia). *Sustainable asymmetric organocatalysis in water and sub- or supercritical carbon dioxide.*

14:30 – 15:00 Closing remarks

15:00 Discussion, outlook and future plans

SPEAKERS

Professor Valentine P. Ananikov



Co-Chairman of the seminar

Elected Member of Russian Academy of Sciences

Head of Laboratory

Zelinsky Institute of Organic Chemistry

Russian Academy of Sciences, Moscow, Russia

Group web-site: <http://AnanikovLab.ru>

Professional areas – catalysis in organic synthesis:

Formation of molecular complexity and development of new transformations using metal complexes and nanoparticles as catalysts. Of special importance is the development of new generations of highly active nanosized and molecular catalysts in the area of fine organic synthesis. Mechanistic studies of chemical reactions by experimental and theoretical methods are employed to uncover challenging topics in catalysis and gain fundamental knowledge about catalytic transformations. Important studies include discovery of “cocktails” of catalysts and revealing the role of dynamic phenomena in catalysis.

Lecture: *Understanding Active Species in Catalytic Transformations: from Molecular Catalysis to Metal Clusters and Dynamic Nanoparticle Systems*

Professor Graham J. Hutchings



Co-Chairman of the seminar

Cardiff University, UK

Regius Professor and Director of Cardiff Catalysis Institute

Professional areas – chemical and environmental catalysis:

Special interest is in gold nanocrystals as novel active heterogeneous catalysts and their characterisation. Supporting gold on graphite or activated carbon makes catalysts that can oxidise alkenes with molecular oxygen under mild conditions. New gold palladium catalysts have been designed that can be used under inherently safe, non-explosive conditions. His group also works on environmental catalysis.

Lecture: *Catalysis using gold-containing nanoparticles*

Catalysis is of crucial importance for the manufacture of the goods and infrastructure necessary for the effective wellbeing of society. Catalysis, and in particular selective redox catalysis, continues to play a key role in the manufacture of chemical intermediates and there is a continuing requirement to design new effective redox catalysts. The identification that gold in nanoparticulate form is an exceptionally effective redox catalyst has paved the way for a new class of active catalysts. Gold is the most active catalyst for the oxidation of carbon monoxide at ambient temperature. It is also the most effective catalyst for the synthesis of vinyl chloride by acetylene hydrochlorination. Gold has recently been commercialized in China for this reaction. The synthesis of active catalysts will be described as well as their characterization. Aspects of the latest research on these topics will be presented.

Professor Valerii I. Bukhtiyarov



Academician RAS, Director, Boreskov Institute of Catalysis Siberian Branch RAS, Head Lab, Head Department, Novosibirsk State University, Novosibirsk, Russia

Professional area – heterogeneous catalysis:

Professor Bukhtiyarov is an expert in the field of heterogeneous catalysis. He studies the chemical processes on solid surfaces with modern *in-situ* physical methods to elucidate «structure-activity» relationships in catalytic systems and develops the techniques for molecular design of nanomaterials for catalytic applications, including reactions for organic synthesis.

Lecture: *Active centers in heterogeneous catalysts: formation and study with in situ methods*

In the recent years a widespread currency in heterogeneous catalysis has been gained by the fundamental approach to the development of the new catalytic systems, which differs from the traditional empirical strategy in that the molecular design (controlled synthesis) of the active component is preceded by an in-depth study of the mechanisms of the catalytic reactions and structure of the active centers. Evidently the efficiency of this approach depends essentially on the level of development of the physical methods for studying the solid, including, first of all, the surface sensitive methods underlying such field of research as Surface Science.

More than thirty years of use of the physical methods of the surface study significantly advanced the understanding of such phenomena as chemisorption, interaction in the adsorption layers, the chemical reactions on the surface of the solid. However, information registered in the conditions of Surface Science experiments ($P < 10^{-4}$ Pa) may have little in common with the real surface of a working catalyst ($P > 10^2$ Pa). To solve this problem the researchers lately undertake the numerous attempts to develop some new or modernize the existing methods to study of the catalyst surface in order to conduct the experiments at a

pressure of real catalysis. The methods able to work at high pressures list polarization-modulation infrared reflection absorption spectroscopy (PM IRAS) and sum frequency generation spectroscopy (SFG), scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), and some others. A special place in this list belongs to the methods of absorption of the X-rays (XANES and EXAFS) as well as X-ray photoelectronic spectroscopy (XPS), which attracts a special attention of the researchers due to its universality.

The given lecture presents a review of the studies of the structure of active centers of the supported metal catalysts immediately in the course of the catalytic reaction, i.e. *in situ*. The reaction of epoxidation of ethylene and oxidation of hydrocarbons are used to demonstrate how the reaction medium changes the chemical and phase state of the active component, and finally forms new adsorption species. The results in this work show that the nature of the active centers performing the catalytic reaction can be determined only when the characterization of the catalyst surface is accompanied with the testing of the catalytic properties (activity and selectivity) by the methods of mass-spectrometry or gas chromatography.

The author thanks RFBR for the financial support (project 17-03-01378A).

Professor Richard Catlow



University College London and Cardiff University, UK

Foreign Secretary of the Royal Society

Professional area – computer models to solid state and materials chemistry:

He develops computer models that investigate the synthesis, structure and properties of materials in the solid phase. By combining his powerful computational methods with experiments, Richard has made considerable contributions to areas as diverse as catalysis and mineralogy.

His approach has also advanced our understanding of how defects – missing or extra atoms – in the structure of solids can result in non-stoichiometric compounds. Richard's work has offered insight into mechanisms of industrial catalyst, especially involving microporous materials and metal oxides. In structural chemistry and mineralogy simulation methods are now routinely used to predict the structures of complex solids and silicates, respectively, thanks to Richard's demonstrations of their power.

Lecture: *Modelling, neutron scattering and synchrotron radiation studies of structure, dynamics and reactivity in catalytic systems*

We will describe how the concerted use of modelling techniques with neutron scattering and synchrotron radiation methods can yield unique information on structures,

dynamics and mechanism in a range of catalytic systems and processes. Our discussion will concentrate on the following systems:

(i) The dynamics and reactivity of hydrocarbons in microporous catalysts where we will illustrate the role of computational modelling in conjunction with neutron scattering techniques.

(ii) The structures and reactivities of oxide supported nano-particulate catalysts, including insights in the re-structuring of nano-particles during catalytic reactions, where we will highlight recent application of synchrotron based techniques.

(iii) The activation of hydrocarbons and carbon dioxide on oxide surfaces, where we shall emphasise the information on key mechanistic aspects revealed by recent QM/MM modelling studies.

We will also consider other areas of catalytic science where the synergistic use of modelling with X-ray and neutron scattering techniques could be fruitfully applied.

Professor Victor Chernyshev



Platov South-Russian State Polytechnic University (NPI), Chemical Technologies Department

Director of the Research Centre “Nanotechnologies”, Novochoerkassk, Russia

Professional area - heterocyclic compounds:

Research interests include heterocyclic compounds, metal complexes of N-heterocyclic carbenes, transition-metal catalysis, plant biomass conversion into chemicals and fuels, biorefinery.

Lecture: *Conversion of carbohydrates to 5-hydroxymethylfurfural and furan-derived monomers for new generation of polymers and functional materials*

Dr Jennifer Edwards



Cardiff University, UK

University Research Fellow

Professional area – design and application of catalysts based on precious metals:

Jennifer’s research specialises in the use of supported metal nanoalloys for a range of reactions with particular emphasis on the direct synthesis of hydrogen peroxide.

Lecture: *Novel catalysts for H₂O₂ synthesis and their utilisation in wastewater treatment*

The direct synthesis (DS) of hydrogen peroxide from H₂ and O₂ presents an atom

efficient route to an important commodity chemical if the reaction proceeds with high H_2 selectivity. Supported bimetallic nanoparticles are known to be highly active and selective for this reaction. The composition of the particles, catalyst support and reaction conditions result in catalysts with $<99\%$ H_2 selectivity, and materials which do not over hydrogenate the H_2O_2 formed to water¹.

Modification of the catalyst preparation route results in materials with varying hydrogenation activity. This is beneficial in some cases (wastewater treatment), and detrimental in others (high conc of H_2O_2).

One potential application of the direct synthesis process is to produce H_2O_2 in quantities sufficient to eradicate bacteria present in a greywater stream. Roughly 50% of the average household's water is greywater (effluent originating from washing machines, dishwashers etc) and it's possible a small system capable of producing H_2O_2 in this stream would be enough to reduce harmful microorganisms present so the water can be reused within the household. For such system to be viable, the H_2O_2 would need to be formed under challenging conditions (ambient temperature, pressure in a water only solvent system) and it is likely new catalyst formulations will be required (where H_2O_2 is catalytically decomposed to radicals).

[1] Edwards, J. K. *et. al.*, *Science* **2009**, 323, 1037.

Dr Emma Gibson



University of Glasgow, UK

Research fellow

Professional area and experience - Most recently, she was using Raman spectroscopy for the non-invasive investigation of catalyst extrudates during the impregnation and drying steps of their preparation. Prior to this she studied steam reforming catalysts under operando conditions using FTIR.

She has also investigated the solid state interactions of amine hydrochloride salts using single crystal XRD, FTIR and INS spectroscopy.

Lecture: *Developments in advanced in situ and operando spectroscopy for catalysis*

Synchrotron radiation sources offer powerful techniques, which can be used to study catalyst under working conditions. Two case studies are used to demonstrate the use of XAFS (X-ray absorption fine structure) for *operando* catalyst studies. Firstly, a non-thermal plasma-assisted (NTP) catalytic reaction was studied under *operando* conditions to determine by which mechanism NTPs can assist CH_4 oxidation.¹ In a second example, DRIFTS (diffuse reflectance infrared Fourier transform



***In situ* XAFS set up to study, the NTP assisted CH_4 oxidation**

spectroscopy) is used in combination with XAFS to provide both surface sensitive information and local structure changes during the restructuring of a AuPd bimetallic catalyst under operando conditions.²

[1]. E. K Gibson, C. E Stere, B. Curran-McAteer, G. Cibir, D. Gianolio, A. Goguet, P. P. Wells, C. R. A. Catlow, P. Collier, P. Hinde, C. Hardacre, *Angew. Chem.* **2017**, 129, 9479 – 9483.

[2]. E. K. Gibson, A. M. Beale, C. R. A. Catlow, A. Chutia, D. Gianolio, A. Gould, A. Kroner, K. M. H. Mohammed, M. Perdjon, S. M. Rogers, P. P. Wells, *Chem. Mater.* **2015**, 27, 3714–3720.

Professor Yulia Gorbunova



Corresponding member of Russian Academy of Sciences

Kurnakov Institute of General and Inorganic Chemistry, Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia

Leading scientist

Professional area – Supramolecular materials, Coordination chemistry, Molecular switches, Macrocyclic compounds, Tetrapyrroles, Lanthanides.

She is Vice-President of the Mendeleev Russian Chemical Society; Russian representative in Society of Porphyrins and Phthalocyanines; Russian representative in European Association for Chemical and Molecular Science (EuCheMS), Inorganic Chemistry Division.

Lecture: *Molecular switches based on tetrapyrrolic compounds*

Functional properties of such macrocyclic tetrapyrrolic ligands as porphyrins and their derivatives are widely exploited in natural and artificial systems. The molecular structure of free base porphyrins and their complexes can be precisely adapted to the target function and the operating environment by varying the substituents on the macrocycle. Another tool widely used by Nature to increase the functional performance of tetrapyrroles is the coordination and supramolecular chemistry approaches. Such approaches lead to wide range of application of synthetic porphyrins and their analogues.

From other side, the possibility to control and tune the properties of a single molecule attracts scientists from ancient times to our days. This is well confirmed by the Nobel Prize in Chemistry in 2016 that was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa "for the design and synthesis of molecular machines".

In this report the recent results of our group concerning development of molecular materials, switches and machine based on porphyrins and phthalocyanines will be discussed in the context of its application¹⁻⁹ including catalytic ones¹⁰.

[1]. Gorbunova, Y.G., Grishina, A.D., Martynov, A.G. et al. *J. Mater. Chem. C*, **2015**, 3, 6692.

- [2]. Safonova, E. A., Martynov, A. G., Zolotarevskii, V. I. et al. *Dalton Trans.* **2015**, *44*, 1366.
- [3]. Safonova, E. A., Martynov, A. G., Nefedov, S. E. et al. *Inorg. Chem.*, **2016**, *55*, 2450.
- [4]. Meshkov I.N., Bulach V., Gorbunova Yu.G. et al. *Inorg. Chem.*, **2016**, *55*, 10774.
- [5]. Polovkova M.A., Martynov A.G., Birin K.P. et al. *Inorg. Chem.*, **2016**, *55*, 9258.
- [6]. Enakieva Yu.Yu., Volostnykh M.V., Nefedov S.E. et al. *Inorg. Chem.*, **2017**, *56*, 3055.
- [7]. Oluwole, D.O., Yagodin, A.V., Mhkize, N.C. et al. *Chem.- A Eur. J.*, **2017**, *23*, 2820.
- [8]. Meshkov, I.N., Bulach V., Gorbunova, Yu.G. et al. *Chem. Commun.*, **2017**, *53*, 9918.
- [9]. Lapkina, L.A., Larchenko, V.E., Kirakosyan, G.A. et al. *Inorg. Chem.*, **2017**, DOI:10.1021/acs.inorgchem.7b01983
- [10]. Kroitor A.P., Cailler L.P., Martynov A.G. et al. *Dalt. Trans.*, **2017**, DOI: 10.1039/C7DT03703A

Dr Andrew Logsdail



Cardiff University, UK

University Research Fellow

Professional area - computational modelling of heterogeneous catalysis:

Andrew's current research involves development and application of novel methods to model the properties of catalytic materials and/or catalyst supports. His interests include structural modelling of gold nanoparticles and bimetallic derivatives, metal-nanoparticle based catalysis, and defect modelling in metal oxide catalytic materials.

Lecture: *A computational materials perspective on heterogeneous catalysis*

As consumer desire for affordable, clean, renewable energy continues to grow, despite increasingly stringent environmental legislation, heterogeneous catalysis is vital to ensure environmental viability. In many cases, progressively more efficient heterogeneous catalysts have been produced and tested experimentally, but a fundamental understanding of the reaction mechanisms and material properties that make these catalytic processes effective remains elusive.

To aid our understanding in this field, computational chemistry has become a necessary tool for providing accurate descriptions at a molecular level, particularly due to the recent theoretical improvements in fields such as electronic structure theory, as well as from the continued growth in accessible computational resources. We present our work applying

computational chemistry techniques, including the embedded-cluster QM/MM methodology,^{1,2} in the context of heterogeneous catalysis. Particular focus is towards elucidating catalytic mechanisms, understanding the effects of reaction environments, and characterizing the underlying properties of important materials, such as TiO₂, at the atomic level (Figure 1).³ The materials are considered both as catalysts and as supports for metal nanocatalysts, with superior photocatalytic activity for AuPd/TiO₂, over individual components, justified using materials chemistry concepts. [4]

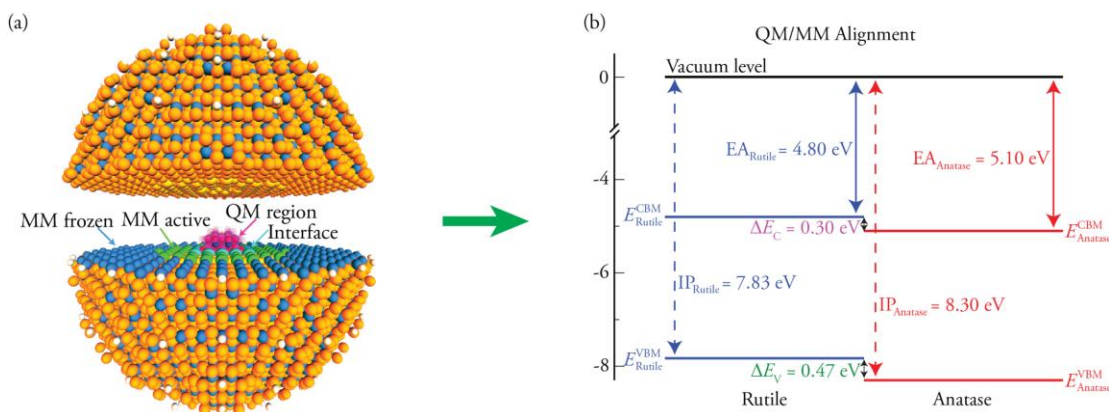


Figure 1: **(a)** Graphic of a hybrid QM/MM embedded cluster as used for rutile TiO₂. The cluster is divided into hemispheres to highlight the different regions in the model. Hole density iso-surfaces are shown (semi-transparent purple) in the QM region. **(b)** Schematic of the QM/MM alignment of rutile and anatase TiO₂. IP and EA denote ionization potential and electron affinity, respectively. The electron affinity is calculated by adding the experimental bandgaps to the calculated ionization potentials. ΔE_V and ΔE_C are the valence band offsets and conduction band offsets, respectively and E^{CBM} and E^{VBM} denote the positions of the conduction band and valence band respectively.

[1]. “The Nobel Prize in Chemistry 2013”, Royal Swedish Academy of Sciences, October 9, 2013

[2]. P. Sherwood *et al.*, J. Mol. Struct.: THEOCHEM. (2003), 632, 1

[3]. D. O. Scanlon *et al.*, Nature Mater. (2013), 12 (9), 798

[4]. Su *et al.*, ACS Nano (2014), 8 (4), 3490

Professor Russell Francis Howe



University of Aberdeen, UK

Chair of Materials Chemistry

Professional area - Applications of neutron spectroscopy to zeolite catalysis, EPR spectroscopy of semiconductor photocatalysts, as well as infrared microspectroscopy with synchrotron radiation.

Lecture: *Operando Infrared Spectroscopy on Zeolite Catalysts Using*

Synchrotron Radiation

The conversion of methanol to hydrocarbons over acid zeolites, particularly ZSM-5 or SAPO-34, has attracted widespread attention since its first commercial implementation in New Zealand in 1985 and more recent plant constructions in China. There is general agreement that the formation of hydrocarbons over the working catalyst proceeds via a so-called hydrocarbon pool (HCP): a reservoir of hydrocarbon species within the zeolite pores undergoes methylation, cyclisation and cracking to form the broad distribution of C₂ to C₁₀ hydrocarbons found in the product stream. How this hydrocarbon pool is formed however from methanol i.e. how the first carbon-carbon bonds are formed, remains a matter of mechanistic speculation.

Infrared spectroscopy is widely used to probe adsorbed species in zeolite catalysts. The ~ 2 orders of magnitude brightness advantage of a synchrotron source over a laboratory infrared source means that good quality infrared spectra can be obtained in an infrared microscope from areas as small as 10 x 10 microns allowing distribution of species within crystals to be mapped. We have previously applied the method to study CO₂ uptake in MOF single crystals and showed also that orientation of adsorbed molecules can be deduced from polarization studies.^{1,2} In this talk a further advantage of synchrotron microspectroscopy will be illustrated: by coupling an in-situ reaction cell to rapid scanning mass spectrometer analysis of effluent gases we have been able to observe on a time scale of < 1 second the evolution of adsorbed species when methanol or dimethylether first encounters an individual crystal of the catalyst, and to correlate these species with the first generation of olefin and aromatic products.

Experiments have been conducted with methanol at different temperatures, with methanol-d₄ and with dimethylether, to build up a complete picture of species present in the zeolite pores and how these relate to the downstream products detected by MS. From these data it is now possible to outline a reaction scheme in which methanol is initially converted via dimethylether into an olefinic HCP species which further evolves into aromatic HCP species with temperature and time on stream. The microscale of the experiment and the signal to noise achieved with a synchrotron infrared source has allowed spectral changes to be monitored on a time scale much shorter than has been possible in conventional infrared experiments.

[1]. Eschenroeder, E. C. V.; Turrina, A.; Picone, A. L.; Cinque, G.; Frogley, M.D.; Cox, P. A.; Howe, R.F.; Wright, P.A.: , “ Monitoring the Activation of Copper-Containing Zeotype Catalysts Prepared by Direct Synthesis Using in Situ Synchrotron Infrared Microcrystal Spectroscopy and Complementary Techniques. “, *Chemistry of Materials*, **26**, 2014, 1434-1441.

[2]. Greenaway, A.; Gonzalez-Santiago, B.; Donaldson, P. M.; Frogley, M.D.; Cinque, G.; Sotelo, J.; Moggach, S.; Shiko, E.; Brandani, S.; Howe, R.F.; Wright, P. A, “In situ Synchrotron IR Microspectroscopy of CO₂ Adsorption on Single Crystals of the Functionalized MOF Sc₂(BDC-NH₂)₃”,. *Angewandte Chemie International Edition*, **53**, 2014, 13483-13487.

[3]. Howe, R.F. Suwardiyanto, Price, D.J., Castro, M., Wright, P.A., Greenaway, A., Frogley, M.D., Cinque, G. “Reactions of Dimethylether in Single Crystals of the Silicoaluminophosphate STA-7 studied via *Operando* Synchrotron Infrared Microspectroscopy “, *Topics in Catalysis*, in press (2017).

Professor Anton Maximov



A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

Acting Director

Professional area - homogeneous and heterogeneous catalysis of petrochemical and refining processes, special fuel production processes:

Nano-heterogeneous catalysis of hydrogenation, hydrodearomatization, hydroisomerization, hydrocracking processes; petrochemical processes in two-phase systems and in alternative solvents over immobilized metal complexes and supramolecular catalysts.

Lecture: *Slurry-phase hydroprocessing using ultra-dispersed catalysts*

Effective converting low value petroleum feed-stocks into high value fossil fuels is mostly determined by hydroprocessing providing both removal of heteroatomic molecules, and conversion of heavy and aromatic hydrocarbons in middle distillate fractions and in feedstock for petrochemistry. One of possible ways of efficiency improvement of such processes is their carrying out in a slurry or blacking reactors with "pseudo-homogeneous" catalysts based on nano- and meso- size particles of a disperse phase (nanoheterogeneous approach). The catalyst can be used with greater ease in the presence of much heavier feedstocks containing large complex molecules than over a supported catalyst. Slurry-phase hydrocracking with nanosized catalysts is the most suitable technology for the conversion of heavy oils/residues.¹⁻³

We present the results on the nanoheterogeneous approach using transition metal sulfides catalysts for a number of hydroprocesses: hydrodearomatization of high-aromatic

secondary gasoils, hydrocracking of vacuum gasoil, hydrogenations of various types of polymeric and oligomeric substrates, hydrocracking of "biooil".

Possible advantages and challenges of various procedures used for nano- or meso-size catalytically active particles formation (from oil-soluble precursors, from the reverse microemulsions of precursors in hydrocarbon feedstock or special media, such as ionic liquids, from s) are covered. The developing of "dual" catalysts for slurry hydroprocessing using sulfide and conventional heterogeneous acid components of various nature for ensuring hydrocracking is described. The advances of the catalyst recycling in slurry and blacking reactors are discussed

1. Khadzhiev S.N., Kadiev K.M., Yampolskaya G.P., Kadieva M.K. Adv. Coll. Inter.Sci., 2013, 197, 132.

2. Khadzhiev S.N., Maximov A.L., Kadiyev H.M. In book Nanomaterials: properties and perspective applications. - M.: Scientific world, 2014, page 323-348

3. Maximov A., Sizova I., Khadzhiev S. Pure Appl.Chem., 2017, 89(8), 1145

Work is performed at the expense of means of RNF, the project No. 15-13-00123

Dr Laura Torrente Murciano



University of Cambridge, UK

University Lecturer and Leader of the Process Integration and Catalysis Group

Professional area - the integration of processes and development of novel catalytic routes for sustainable technologies.

Specific research interests are within development of 3D printed micro-devices for the continuous production of metal nanoparticles with tuneable sizes to differential reactors for kinetic studies and membrane reactors; integration of reaction and separation steps in chemical processes in multiphasic systems in emulsions and metallic membranes for *in-situ* hydrogen separation; catalytic supports with a focus on the structure-property relationships of a wide range of materials such as ceria, titanate, alumina and magnesia; low temperature activation of molecules, specially methane and CO₂ utilisation; low temperature ammonia decomposition catalysts, integration within the existing PEM fuel cell technology and life cycle analysis.

Lecture: *Manufacturing of designed heterogeneous catalysts*

Metal nanoparticles have stimulated the interest of the scientific community during the last decades due to their unique catalytic, optical, electronic, magnetic, etc. characteristics. These intrinsic chemical and physical properties are strongly dependent on the size and shape of the metal nanoparticles with a huge scientific effort dedicated to the development of

reproducible and reliable synthetic routes. Despite this, their large-scale deployment is currently limited by the lack of manufacturing techniques to ensure tuneable sizes, narrow size distributions and controlled morphologies.

In this presentation, we will present our recent work on the design of a novel manufacturing technology based on micro-tubular reactors for the continuous synthesis of ligands-free metal nanoparticles. We exploit the opportunities offered by the laminar flow regime characteristic of micro-devices to prevent the agglomeration of the particles in the absence of capping ligands, while promoting transitional flows to lead to narrow size distributions. This approach constitutes a departure from previous strategies to narrow the size distribution during the continuous synthesis of metal nanoparticles such as bi-phasic or Taylor flow systems in microreactors which require the use of stabilizing ligands.

By careful design of the reactors geometry guided by computational fluid dynamic (CFD) simulations, we have demonstrated that in curved micro-reactors, Dean vortices are promoted on the cross section of the channels leading to the rotation of the fluid, reducing the residence times distributions. This effect is directly translated into small particles (< 4 nm) with narrow size distributions [4].

In addition, the absence of ligands in the surface of the particles also allows the separation of the seed formation and growth stages. In this way, further addition of silver precursor in a number of reactors connected in series, leads to an exquisite growth control, allowing the production of nanoparticles with selective sizes between 5-20 nm, while conserving the narrow size distributions presented by the original seeds.

We will also demonstrate how this technology can be applied not only to other metals such as gold or palladium particles but also more complex compositions (e.g. perovskite nanocrystals).

Dr Sergey N. Osipov



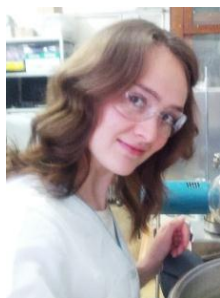
A.N. Nesmeyanov Institute of Organoelement Compounds, RAS, Moscow, Russia

Head Laboratory of Ecological Chemistry

Professional area - synthetic organic chemistry, fluoroorganic chemistry, chemistry of biologically active compounds (amino acids, peptides, N-heterocycles), organometallic chemistry and catalysis.

Lecture: *New Fluorinated Unsymmetrical NHC-Ligands for Metal Catalysis*

Dr. Elena A. Redina



N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

Laboratory of Development and Study of Polyfunctional Catalysts

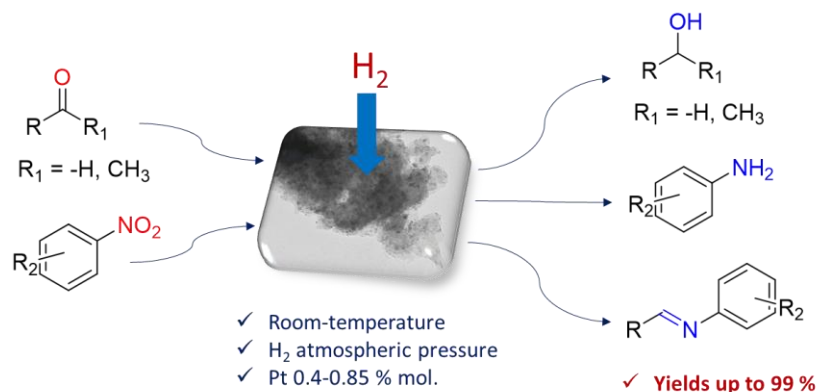
Research Fellow

Professional area - heterogeneous catalysis, catalysis in organic chemistry, catalysis by gold, catalyst preparation, nanochemistry, green chemistry.

Lecture: *Pt-nanocatalysts for selective room-temperature transformations of carbonyl- and nitro-compounds in the presence of H₂*

Hydrogenation reactions are one of the most important types of transformations in synthetic organic chemistry. Selective hydrogenation of carbonyl compounds makes it possible to obtain alcohols of various structures, including unsaturated ones. Hydrogenation of compounds containing nitro groups is used to produce amines, an important class of organic compounds. Today there is a trend to replace conventional methods for the selective reduction of carbonyl and nitro-compounds, which based on the use of stoichiometric reducing agents or homogeneous catalysis on metal complexes with more convenient methods of heterogeneous catalysis. Hydrogenation on heterogeneous catalysts allows a process with a high atomic efficiency to be carried out, wherein the catalyst can be easily separated from the reaction mixture and reused. However, to date, there are no heterogeneous-catalytic systems for performing selective hydrogenation reactions with high activity under ambient conditions.

Herein we report on Pt-based nanocatalysts supported on ceria-zirconia mixed oxides for room-temperature hydrogenation of aldehydes, ketones, nitro-aromatics to the corresponding alcohols and amines in the presence of H₂ at atmospheric pressure. In addition, the catalysts show high activity in one-pot synthesis of imines from nitro-aromatic compounds and aldehydes.



The low-temperature activity and selectivity of the obtained catalysts in the reactions with H₂ was attributed to the formation of active hydrogen species due to intense H₂ spillover on the surface of the catalysts. This effect was observed at temperatures -50-25°C for the first time in this work.

This work was supported by the Russian Science Foundation grant 17-73-20282.

Professor Andrea E. Russell



University of Southampton, UK

Professional area – Physical Electrochemistry:

Her research interests are in the application of spectroscopic methods to study the electrode/electrolyte interface, with particular emphasis on electrocatalysts and electrode materials for fuel cells, metal-air batteries, water electrolyzers, and gas sensors.

She holds the Chair of the Physical Electrochemistry Division of the International Society of Electrochemistry.

Lecture: *In situ X-ray studies of PEM fuel cell electrocatalysts: Bimetallic catalysts for CO tolerance and DAFCs*

Pt-based bimetallic electrocatalysts are used as at the anode of reformat fuelled and direct alcohol PEM fuel cells. XAS can be used to provide characterisation under in situ conditions, which can then be extended to operando studies. In this seminar, results for a series of carbon supported PtRu and PtSn electrocatalysts as a function of the bimetallic composition will be presented, with emphasis on how the electrode potential and presence of adsorbates can change the surface composition of the electrocatalysts.

Professor Duncan Wass



University of Bristol, UK

Professional area – homogenous catalysis:

His specific interest lays in transition metal-containing frustrated Lewis pairs, new catalysts for selective olefin oligomerisation, catalytic upgrading of bioethanol and carbon dioxide, and composite materials with new functionality.

Lecture: *Homogeneous Catalysts for Advanced Biofuels*

The catalytic conversion of biomass-derived feedstocks into more valuable chemical products and fuels is an important objective for a more sustainable future. We have developed a range of homogeneous catalysts for the upgrading of bioethanol and methanol into more advanced biofuel molecules such as isobutanol. These ruthenium-based systems demonstrate outstanding selectivity and mechanistic study has revealed an intriguing balance between competing reaction pathways depending on the specific catalyst structure used. In related work, the same catalysts also proved to be highly productive for the hydrogenation of carbon dioxide to methanol. The use of an amine auxiliary co-catalyst is essential for good performance in this chemistry and the nature of the amine is critical in determining selectivity. This presentation will outline our motivations for studying these systems, and recent results in the area.

Professor Dmitry Yakhvarov



A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences Kazan, Russia

Deputy Director for Science, Chief Researcher

Professional area - electrochemical methods in organic and organoelement chemistry and materials science:

His current research interests are focused on the chemistry and electrochemistry of organometallic species, elemental (white and black) phosphorus, silicon derivatives, homogeneous catalysis, chemistry of highly reactive intermediates, including electrochemically generated phosphane oxide, H_3PO .

Lecture: *Electrochemical reactions of transition metal complexes as a way to new catalysts and materials*

The creation of environmentally safe and ecologically clean chemical technologies is one of the priorities in the synthetic preparation of practically important organic and organoelement compounds. From this point of view the electrochemical methods can be considered as an efficient alternative to the classical synthetic procedures as they proceed in mild conditions and usually involve a cyclic regeneration of the used catalysts.

The performed in our research group investigations allowed elaborating the procedures for electrochemical preparation of the active catalysts for ethylene oligo- and polymerization, which are based on organonickel sigma-bonded complexes ¹, including the recent examples containing bulky substituents in the sigma-bonded aromatic ring ². Our recent investigations are focused on searching and elaboration of the reliable electrochemical ways for generation and activation of organometal catalysts based on N-N ^{3,4} and P-O ⁵ chelating ligands.

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This work is financially supported by the Russian Foundation for Basic Research and the Government of the Republic of Tatarstan (project 15-43-02667).

Professor Sergey Zlotin



N.D. Zelinsky Institute of Organic Chemistry RAS, Moscow, Russia

Deputy Director, Head of N.D. Nazarov Laboratory of Fine Organic Synthesis

Professional area - asymmetric synthesis, sustainable asymmetric organocatalysis, green chemistry, pharmacology-oriented and energetic nitrogen-oxygen systems.

Lecture: *Sustainable asymmetric organocatalysis in water and sub- or supercritical carbon dioxide*

Asymmetric organocatalysis is a rapidly growing area of organic chemistry. Organocatalysts are “greener” than organometal catalysts as they do not contain toxic heavy metals and in many cases are compatible with green reaction media (ionic liquids or water). However, they may be responsible for contamination of products with hardly separable organic impurities. Moreover, most efficient bifunctional chiral organocatalysts are rather expensive and therefore less attractive for industry. These environmental and economical issues may be addressed by the development of immobilized organocatalysts tolerant to green solvents.

We designed a series of novel ionic liquid (IL)-supported catalysts, which allow performing catalytic transformations in the presence of water. In particular, secondary- or tertiary amine-derived IL-supported catalysts containing long-chain spacer groups and/or hydrophobic fluorinated anions appeared useful in asymmetric cross-aldol and Michael reactions under “on-water” conditions¹. Valuable products were generated in these reactions

with excellent diastereo- (dr up to 99:1) and enantioselectivities (up to 99% ee)². Furthermore, the supported catalysts could be reused up to 30 times in the same or similar reactions without a decrease of product yield or selectivity of the reaction.

Another prospective approach to enhance sustainability of organocatalysts is based on the use of sub- or sc-CO₂ as reaction medium. We discovered that 1,3-dicarbonyl compounds, aniline derivatives and diphenylphosphite enantioselectively react with α -nitroalkenes in the presence of bifunctional tertiary amines bearing thiourea or squaramide units in the proposed conditions to afford corresponding Michael adducts or products of their cascade transformations with up to 99% ee. A significant potential of the supercritical extraction for product isolation and catalyst recovery which eliminates the use of organic solvents was demonstrated³.

The developed green procedures were applied to enantioselective synthesized of key precursor to antiepileptic drug (pregabalin), important chiral α -amino acids, β -amino phosphonic acid derivatives, γ -lactones and bioactive tetrahydroquinilines (angustureine and martinelline analogs).

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This research was supported by the Russian Science Foundation (project no. 14-50-00126).

