

Professor Vladimir Zaitsev

Corr.-member of Academy of Sciences of Ukraine, Professor, DSc., PhD

Professor Vladimir Nikolayevich ZAITSEV (was born in 11 Oct. 1958) was graduated in 1981 at Kiev State University (Kiev Ukraine) as inorganic chemists. In 1985 he received his PhD and in 1997 D.Sc. degree (both from Kiev State University). From 1984 he works in Kiev State University (later re-named to Taras Shevchenko National University of Kyiv) as young scientists, assistant and associate Professor. In 2001 he was habilitated to position of full Professor. In 2009 he was elected to National academy of Sciences of Ukraine as a correspondent member in the field of surface chemistry.

Today Prof Zaitsev is internationally recognised leading specialist in the field of surface chemistry of organo-mineral composite materials with aspects of their application in analytical chemistry, catalysis and bio-medicine. His research interest is a harmonious combination of preparation of new organo-mineral hybrid materials, studying of their chemical properties, investigation of specific features of their chemical behaviour, generalization of the results with the purpose of development of new tools and methods for application of such materials. He is an author of about 300 publications with three monographs, four textbooks, 14 patents and about 120 articles in peer-review journals with total Impact Factor of 131 and H-factor of 14. Prof Vladimir Zaitsev is a chairperson of the Scientific Council in analytical chemistry at National Academy of Sciences of Ukraine, a member of European Association for Chemical and Molecular Sciences (EuCheMS), member of scientific advisory committee at Organisation for Prohibition of Chemical Weapons, OPCW (the Netherlands). Vladimir Zaitsev is an editor of scientific journal "Methods and Objects of chemical analysis", member of Editorial Board of next scientific journals: Chemical Papers, Chemistry and technology of water, Journal of Analytical Chemistry, Journal of Chemistry and Physics of Surface, and Pharmakom. He was invited as visiting professor to University of Campinas (Brazil), INSA Lyon (France), Université de Bourgogne, Dijon (France), ESPCI ParisTech (France).

Prof Vladimir Zaitsev conducts his research in the field of inorganic and coordination chemistry from 1982. In 1990 Mrs Margaret Thatcher was visiting Ukraine for the first time. During this visit she offered the British council scholarships to 10 the best Ukrainian young scientists. Mr Vladimir Zaitsev was only one chemist among the winners. It was the beginning of European integration of the young researcher from Kiev University. After six month successful research training in UK, in contrast to many Soviet young scientists leaving the country in that period, he returned to Ukraine and initiated interdisciplinary research in new topic – surface modified electrochemical sensors based on field-effect transistors. He was able to initiate strong collaboration between Ukrainian physicists (Prof Strikha, Dr Shul'ga A.), chemists (Acad. Skopenko V.) and molecular biologists (Acad. Elskaya A., Dr Soldatkin A., Dr Piletsky S.). As the result of his activity he published a pioneer article on immobilisation of biomolecules on silicon surface¹ and reported new principle for development of biosensors² that later was widely developed in USA³. From 90th research interest of Vladimir Zaitsev was concentrated on interfacial phenomenon and particularly on development of chemical methods for immobilization of organic compounds on inorganic carriers. He developed procedures for immobilization different organic compounds on silica⁴ surface including: aliphatic aromatic and heterocyclic amines, such as 2,2-dipyridil and 1,10-phenanthroline, substituted quinolones; metal-binding S,N and N,O-containing ligands such as: 2,6-pyridinedicarboxylic acid, aminodiphosphonic acids; fragments having ion-exchange properties, such as ethylsulfonic acid, phosphonium and ammonium salts. Special attention was given for development of immobilization technique that allows retaining biological activity of native biomolecules. Particularly, novel simple procedure for immobilization of aryldiazonium groups was patented. This procedure allows visually-

¹ Zaitsev V. N. et al., *Analytica Chimica Acta* **1991**, 252 (1-2), 1-6.

² (a) Zaitsev, V. In *New biosensor for DNA analysis*. USSR conference on Chemical Sensors-89, Leningrad, USSR 1989; (b) Soukhan, V. V., Zaitsev V.N., et al. Modification of Water Surface with denaturated DNA for biosensors development. In *Euroanalysis VIII*, Edinburgh, 1994.

³ Crooks M. R. *Chemical Sensors & Interfacial Design*. Gordon research conference, New London, NH 1998

⁴ Zaitsev V.N. *Complexing silicas: preparation, structure of bonded layer, surface chemistry*. Folio: Kharkov, 1997; p 240.

controlled immobilization of almost any biomolecule from their water solution. About 15 years later this idea was widely anticipated.⁵

In his earlier research work⁶ Vladimir Zaitsev discovered that immobilized ligands react with metal ions in solution differently than they do it in their native state. So in collaboration with Professor Kholin (Kharkov) he concentrated his attention on investigation of interfacial interaction between metal ions in solution and immobilized ligands.⁷ This was a pioneer research. Regardless that this phenomenon not yet fully resolved a model describing complex formation in an interfacial layer was proposed.⁸ This model introduced two new parameters describing objects with immobilized ligands: evolutionary and topographic inhomogeneity. By considering these parameters, some peculiarities of metal binding organo-silicas could be explained and vice-versa - from experimentally observed metal adsorption properties of the organo-mineral hybrid materials composition and structure of immobilized layer can be evaluated. For example, it was observed that protolithic properties of organo-silicas depend from the concentration of bonded groups and their local density. He investigated these effects for different surface-modified materials to understand correlation between bonded layer composition and properties. He realized that the problem is complex and can be solved in strong collaboration and he worked to build such collaboration. He invited scientists from all over the world to deliver lectures and seminars in Ukraine. In 1994 he managed to organize the first Ukraine-USA Summer School on Chemistry & Physics of Surfaces and to get support from International Science Foundation (USA). It was probably the first international conference in science in independent Ukraine.

In 1994 Vladimir Zaitsev applied for Fulbright fellowship and received the grant for 6 months research training with Prof D. Bergbreiter at Texas A&M University, USA. During his stay in USA he not only conducted research but also deliver seminars at Pacific North-West Lab, Hoechst Celanese Corporation, University of Oregon, University of Washington and at Pittsburgh University, where he met Prof J. Yates – well known specialist in surface chemistry, who later several times visited Vladimir Zaitsev's lab in Kiev. It was the period when Professor F. A. Cotton and Professor A. Clearfield use to work in Texas A&M. Because of Prof Zaitsev research profile (coordination chemistry and chemistry of adsorbents) he had productive meetings in Texas with both scientists. During these meetings the idea of combinatorial synthesis of organo-mineral materials was developed.⁹ This approach allows him to obtain a set of materials with similar composition and then study their properties by using earlier developed model. Vladimir Zaitsev used combinatorial synthesis to study reactivity of immobilized amines in reaction of acylation using different cross-linking reagents and transform them to silicas with immobilized hydroxamic acid derivatives. The reactivity was evaluated from the acids yield in their specific reaction with V(V) and Fe(III). The research demonstrated that chemical properties of the materials with immobilized organic fragments depend not only from the nature of immobilized groups but also from their topography (distribution on the surface) and geometry of the immobilized layer.

The 1990th were not a good time for science in Ukraine. On his return to Ukraine Prof Zaitsev tried to secure research potential of his group and makes all possible stress to international collaboration. Particularly in 1993 he won “emergency” grants and in 1994-95 “Long-term research grant” from International Science Foundation for his research group. Prof Zaitsev was able to initiate collaboration with research teams from Uzbekistan, Moldova, Ukraine, Switzerland, UK and France. With IFREMER (France) he proposed new research topic for development of silica-based non-attendant luminescent sensors. The proposed topic and quality of the research team were good enough to get three-year research grant from INTAS (94-2522). Later, because of his state-of-art research and high qualification, he was able to build sustainable network with scientists from UK (Prof J. Evans, Southampton; Prof A. Turner,

5 Mahouche-Chergui S. et al. Aryl diazonium salts: a new class of coupling agents for bonding polymers, biomacromolecules and nanoparticles to surfaces. *Chem. Soc. Rev.* 2011, 40, 4143-4166

6 Skopenko V. V.; Trofimchuk A. K.; Zaitsev V. N. *Zhurnal Neorganicheskoi Khimii* 1982, 27 (10), 2579-2585.

7 Kholin Y. V., Zaitsev V. N., *Metal complexes on chemically modified silica. Folio: Kharkov*, 1997; p 135

8 Kholin Y.; Zaitsev V. *Pure and Applied Chemistry* 2008, 80 (7), 1561-1592

9 Bergbreiter D. E.; Zaitsev V. N. et al. *Combinatorial synthesis of silica-supported metal binding agents and sensors. In Fundamental and Applied Aspects of Chemically Modified Surfaces*, Blitz, J. P.; Little, C. B., Eds. *Royal Soc Chemistry: Cambridge*, 1999; pp 353-360.

Cranfield), France (Prof J. Fraissard, Paris; Prof A. Walcarius, Nancy; Prof S. Szunerits, Lille; Prof D. Barbier and Dr. V. Lysenko, Lyon), Spain (Prof S. G. Granda, Oviedo), Italy (Dr R. Raiteri, Genova), Israel (Y. Nemirovsky, Haifa) and USA (Prof D. Bergbreiter, College Station). This scientific network helps Vladimir Zaitsev to perform high quality research in Ukraine and obtain several INTAS grants: INTAS-1116(1997-2000), INTAS-291(2000-2003), INTAS-7729 (05-08). Together with two Science for Peace grants from NATO: SfP 97-1896 (1999-2001) and SfP 981786 (2006-2009) it allows Prof Zaitsev protect his research group from crushing, purchase scientific equipment and improve scientific quality of the research.

From 1995 Dr Vladimir Zaitsev concentrated his effort on investigation of interfacial metal-ligand interaction. He systematically studied influence of the following factors on the bonded materials properties: a) local density of bonded groups, b) topography of the bonded groups on the surface, c) distance for the functional centre from the surface (geometry of bonded groups), d) the porosity and the surface area of the support, and e) the nature of the immobilised ligands. He found that all these parameters have influence on composition, structure and stability of immobilized metal complexes. So by studying the later one he tried to learn structure of immobilised layer. For example, he found that organosilicas with immobilised heterocyclic and aliphatic amines have highly uniform density of bonded layer where neighbouring fragments interacts with each other. It is so-called cluster distribution of bonded groups. He prove that such structure is dominates among organosilicas. He also was found the reason for existence of two (pK_1 and pK_2) protonation constants for organosilicas with immobilised aminopropyl groups and proposed how to use their values to evaluate a density of the group in the cluster (pK_1) and their concentration (pK_2). Knowledge about structure of bonded layer allows Prof Vladimir Zaitsev predict metal-binding properties of modified silicas and explain structure of immobilised coordination compounds. Particularly, he proved domination of multi-point bindings of metals by immobilised ligands with formation of MQ_2 and even MQ_3 (where Q- is immobilized ligand) complexes. This fact was further used to plan preparation of catalytically active metal complexes.

In 2000 Vladimir Zaitsev was invited for a month to Brazil to deliver a set of seminars in University of Campinas and in 2004 he was invited as visiting CNRS scientists to perform 10 months research in INSA Lyon under a new research project in chemistry of porous silicon. Though surface chemistry of new materials based on porous silicon and silicon carbide was included to scientific attention of Prof Vladimir Zaitsev from 2005. He studied surface chemistry of Si and SiC^{10} particles and developed procedures for their stabilisation and chemical modification.¹¹

Scientific background used in preparation of new advanced materials is used for their application in adsorption and catalysis, in development of new analytical reagents and phases, for development of delivery system for controlled drug transportation and release, for microfluidic systems and chemical sensors, to produce nanosize and nanostructured materials.

For example, organo-silicas with immobilised strong chelating groups such as: 2,6-pyridinecarboxylic, aminodiphosphonic and hydroxamic acids, bis-(dialkyl)-phosphotriamide and 1,10-phenanthroline were studied as adsorbents for water decontamination¹² and analysis; highly selective adsorbents for Cs pre-concentration were proposed and studied for purification of water contaminated with radioactive Cs ions¹³. It has been shown that up to 98% of Cs can be uptaken with Cs/K selectivity of 10^8 .

Organo-mineral materials are very promising in their application as selective membranes for chemical sensors. For example, it was demonstrated that immobilised Heme proteins can have direct electron transfer and peroxidase activity¹⁴. This idea was further developed to obtain very sensitive electrochemical sensors.¹⁵ Immobilisation of Eu on silica-based transparent membrane allows developing chemical sensor for monitoring of food contamination by

10 Alekseev S. A.; Zaitsev V. N. et al. *Chemistry of Materials* 2007, 19 (9), 2189-2194.

11 (a) Chapron J. et al. *Sensors and Actuators B*. 2007, 120 (2), 706-711; (b) Shmigol I. V. et al. *J. of Mass Spec.* 2009, 44 (8), 1234-1240.

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13 Zaitsev V. N. et al. *Analytica Chimica Acta* 1992, 256 (2), 323-329.

14 Nadzhafova O. Y.; Zaitsev V. N. et al., *Electrochemistry Communications* 2004, 6 (2), 205-209.

15 Mazurenko I. et al. *Carbon* 2013, 53, 302-312

antibiotics. This research was supported by EU FP7 IRSES project No. 247603. Based on multilayer porous silicon chemical sensors can be used for monitoring of air on its contamination with chlorinated solvents.^{11a} Other prospective application of porous silicon is devised for microfluidic systems¹⁶ and support for MALDI mass-spectrometry of biomolecules.^{11b} Other important application of developed materials is catalysis. For example, silica with immobilised ethylsulfonic acid demonstrates better activity and selectivity than commercial Amberlyst-15 in ETBE synthesis and at lower temperatures¹⁷. Correct immobilisation procedure of Keggin heteropolyacids ensured excellent dispersion of HPA on the surface, their high thermal stability and so catalytic activity.¹⁸ Recent idea of Prof Zaitsev is application of porous Co-modified SiC in Fischer-Tropsch synthesis was supported by EU by FP7 IRSES grant No. 319013.

Biomedical application of organo-mineral materials is based on their ability to deliver drugs¹⁹. Optimisation of immobilised layer composition can stabilise the target biomolecule and release it under controlled conditions.²⁰ Prof Zaitsev research in the field of fabrication of particles with photo receptors for their bio-analytical application such as controlled drug delivery was supported by EU FP7 grant IRSES no. 269099.

Professor Vladimir ZAITSEV demonstrates advanced organising skills. In 2006 he initiated a foundation of a new peer-review scientific journal "Methods and objects of chemical analysis" and became its editor-in-chief. The journal is published quarterly and has printed and electronic formats (www.moca.net.ua). Professor Vladimir Zaitsev organised in Ukraine several international schools and conferences with active participation of well-recognised scientists. Particularly, in 1994 he chaired "Ukraine-USA Summer School on chemistry & physics of surfaces" supported by NSF (USA) with Bergbreiter D.E., Ferguson G., White J, Yates J.T., Jr. and several other scientists from USA. In 2002 with INTAS support he organised five-day international conference and summer school titled: "New functional materials in chemical analysis" with more than 100 participants, and in 2005 largest chemistry conference in Ukraine: "Analytical chemistry and chemical analysis, AC&CA with 400 participants from 21 countries. He was invited to make oral presentations on many international conferences including: IUPAC (Switzerland, 2012), EUROANALYSUS (2011 Serbia, 2009 Austria, 2007 Holland, 2004, Salamanca), Symposium on Theoretical and Experimental Studies of Interfacial Phenomena and their Technological Application (2010, Poland), 1st Latin America conference on Bioinorganic chemistry (2008, Brazil), PITTCON (2004 and 2007, USA), 9th International conference on fundamental of adsorption (2007, Italy), ARGUS (2007, Russia), ICAS (2006, Russia), Euroensors (2005), AC&CA (2005, Ukraine), 13 International Congress on Catalysis (Paris, 2004), XVII Mendeleev Congress (2003, Russia), Silica 2001 (France), ICCS (2000, UK).

Vladimir Zaitsev group is probably the only one group in Ukraine that regularly accept French students for 3 months training for the period of last five years.

16 Mery E. et al. *Physica Status Solidi C* Vol 6, No 7 2009, pp 1777-1781.

17 Alekseev S. A.; Zaitsev V. N. et al. *Adsorption Science & Technology* 2004, 22 (8), 615-625

18 Kovalchuk T. V.; Sfihi H.; Zaitsev V. N.; Fraissard J.. *Catalysis Today* 2011, 169 (1), 138-149.

19 Mazur M. et al. *Nanoscale* 2013, 5 (7), 2692-2702.

20 Turcheniuk K. et al. *Nanoscale* 2013, accepted for publication.