Russian Chemical Reviews **76** (6) 489 – 491 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n06ABEH003730

Chemical research at the Siberian Branch of the Russian Academy of Sciences

This issue is devoted to the 50th anniversary of the Siberian Branch of the Russian Academy of Sciences the foundation of which was an outstanding event in the history of Russian science. The intensive exploration of Siberia including mineral resources and development of industry and agriculture, which started in the 1950s and was preceded by evacuation of many factories and scientific institutions from the USSR central regions to Siberia during the World War II, brought about numerous problems to be solved by Russian science. This required creation of an adequate scientific potential of Siberia. Outstanding scientists, Academicians M A Lavrentiev and S A Khristianovich proposed the foundation of a new scientific centre in Siberia. The government supported this proposal and on May 18, 1957, the USSR Council of Ministers established the Siberian Branch of the USSR Academy of Sciences, which was the first regional Branch of the Academy. The Siberian Branch comprised the already existing West-Siberian, East-Siberian, Yakutia and Far Eastern (remained a part of the Siberian Branch of the USSR Academy of Sciences up to 1970) subsidiaries of the USSR Academy of Sciences.

From the very beginning, the activity of the Siberian Branch (SB) was based on advanced principles, which have not still lost their value. These include interdisciplinary fundamental research, integration of science and education and development of the required infrastructure for the practical implementation of scientific achievements, the famous 'Lavrentiev triangle'.

As soon as the first year of existence of the SB of the USSR Academy of Sciences, it was decided to establish a number of chemistry-oriented institutes in Siberia, namely, the Institute of Chemical Kinetics and Combustion, the Institute of Inorganic Chemistry and the Institute of Organic Chemistry in Irkutsk. However, the first chemistry-oriented Institute of the Academy appeared in Siberia back during World War II (in 1943). This was the Chemicometallurgical Institute founded in Novosibirsk, together with four other Institutes of the Academy within the bounds of the West-Siberian subsidiary of the USSR Academy of Sciences. Today, this institute is called the Institute of Solid State Chemistry and Mechanochemistry of the SB RAS and is among the eleven actively functioning chemical institutes of the Siberian Branch of the RAS, six of which are located in the Novosibirsk Akademgorodok and refer to the Novosibirsk Scientific Centre of the SB RAS. These are the Joint Institute of Catalysis comprising the G K Boreskov Institute of Catalysis, St Petersburg and Volgograd Branches of the Institute, and the Institute of Problems of Hydrocarbon Processing; the A V Nikolaev Institute of Inorganic Chemistry, the N N Vorozhtsov Novosibirsk Institute of Organic Chemistry, the Institute of Chemical Kinetics and Combustion, the International Tomography Centre, and the above-mentioned Institute of Solid State Chemistry and Mechanochemistry. The rest are parts of other scientific centres of the SB RAS, namely, the Irkutsk (A E Favorsky Irkutsk Institute of Chemistry), Krasnoyarsk (Institute of Chemistry and Chemical Technology), Tomsk (Institute of Oil Chemistry) and Omsk centres (Institute of Problems of Hydrocarbon Processing); the most recently founded Institute for Problems of Chemical and Energetic Technologies is situated in Biysk.

The largest one is the Institute of Catalysis whose staff counts almost 1000. The Institute is a leader in the research of catalytic processes. The works of its founder and the first Director, Academician G K Boreskov, and his school are known all over the world. Boreskov's rule of approximate invariability of the specific catalytic activity of chemicals with invariable chemical and phase composition has underlain the modern theory of heterogeneous catalysis. The Institute's works on mathematical modelling of catalytic processes and development of the strategy for switching from laboratory studies to industrial scale production changed fundamentally the approach to the design of catalytic reactors and prompted the ways for increasing the efficiency of existing industrial processes. A large contribution to the development of physical methods for investigation of catalysts and elaboration of nontraditional ways for performing catalytic reactions was made by Academicians K I Zamaraev and V N Parmon and their co-workers. In particular, they determined the structure of numerous active catalytic sites, developed the methods for stimulation of catalytic processes with light or ionising radiation. Among recent, practically valuable achievements of the Institute of Catalysis, mention should be made of the development of highly efficient titanium – magnesium catalysts for the preparation of a superstrength polymer: ultrahigh-molecular-mass polyethylene. A priority trend in the Institute's activity is the development of environment-oriented processes, in particular, numerous catalytic processes for detoxification of wastes from industry, power engineering and transport.

The history of foundation and development of the Institute of Chemical Kinetics and Combustion (ICKC) is tightly connected with the names of Academician V V Voevodsky, a founder of chemical radiospectroscopy in the USSR, and first Director of the Institute, Corresponding Member of the USSR Academy of Sciences A A Koval'sky. Chemical radiospectroscopy and related studies of the magnetic interactions of molecules, the effect of magnetic field on chemical reactions and the synthesis of stable radicals and molecular magnets are essential priority lines in the research of this Institute. Under direction of Academician Yu D Tsvetkov, the first USSR and European electron spin echo spectrometer specially adapted for investigation of paramagnetic crystals at cryogenic temperatures was devised at the ICKC in 1965. New modifications of the electron spin echo spectroscopy designed and developed at the Institute allow one to study the motion of spin-labelled lipid molecules in biological membranes, the permeability of these membranes, to determine protein conformations and to study electron transfer at the photosynthesis centres. Quantum beats spectroscopy in recombination fluorescence was also developed at the ICKC. This method allows one to study superfast processes in radical ion pairs taking place in solutions over billionth of a second. The works dealing with spin

chemistry carried out at the Institute under the supervision of Academicians Yu N Molin and R Z Sagdeev have gained broad recognition. Studies of the combustion processes in gases and combustion of energetic materials is yet another important scientific trend in the activity of the ICKC. Of special note are works dealing with filtration combustion of gases. In addition, the mechanisms of photochemical reactions and the reactivity of active intermediate species are studied at the Institute. Using a laser on free electrons designed at the G I Budker Institute of Nuclear Physics of the SB RAS, an original method for the investigation of biological macromolecules using terahertz radiation, which does not destroy large molecules, has been developed.

A number of international scientific centres were organised at the base of the Siberian Branch institutes that occupy leading positions in their field of science. One of these centres, the International Tomography Centre (ITC), was founded in 1996 under initiative of Academician R Z Sagdeev in cooperation with the Bruker group of companies. The key lines of research of the ITC include the theory of chemical bond, the reactivity of chemical compounds, the mechanisms of chemical reactions; magnetic phenomena in chemistry and medicine, spin and exchange phenomena, in particular, those in multispin coordination compounds; diagnostic NMR imaging and NMR microtomography for physicochemical applications. The unique 3D MYUR procedure developed at the ITC allows visualisation of the peristaltic motion dynamics of free fluid along the hollow biostructures and direct estimation of the physiological rhythm parameters. The development of new contrasting means based on stable aminoxyl radicals for magnetic resonance imaging (MRI) of living organisms is in progress. Magnetic resonance imaging is widely used for chemical investigations, as it makes it possible to study the internal structure and behaviour of samples without their destruction. The method has been successfully used for *in situ* studies of mass transfer within porous materials and also for studies of gas and liquid structure. Using aminoxyl radicals and paramagnetic metal ions, the researchers of the ITC were able to prepare heterospin coordination compounds, which represent a new type of molecular magnets. Pioneering studies on the design of layered polymeric and framework structures were carried out at the ITC. A new in principle class of objects was discovered, the so-called breathing crystals, which tend to change their volume unusually strongly around magnetic transitions upon temperature variation.

A key trend in the activity of the A V Nikolaev Institute of Inorganic Chemistry (NIIC) is the physicochemical research of materials for electronics. A research group of the Institute headed by Academician F A Kuznetsov carried out a large series of works in this field, in particular, they developed the strategy of chemical vapour deposition, which is among the techniques most widely used in industry for the manufacture of microelectronic devices. Yet another important project of the Institute is the development of a crystal growth process for laser technology by the Chokhralsky low-gradient method. A new trend in the NIIC activity is supramolecular chemistry concerned with large molecular arrays self-assembled from geometrically and chemically complementary fragments. Typical examples of supramolecular compounds are 'host – guest' complexes. These complexes are studied at the Institute, in particular, transition metal complexes incorporated into a hydrophobic cavity of large molecular containers, cucurbiturils. It was shown experimentally that the molecules that get in the cavity of such a molecular container can change essentially their physicochemical properties. This method can be used to prepare complexes containing metals in unusual oxidation states with unique reactivity. At the Institute, a method has been developed and a table-top spectrometer NMR-micro has been designed for nanosystem porometry and for studying the dynamics of nanoliquids under quantum constraint conditions and the properties of the mobile subsystem in ultrathin channels of nanoporous items and heterostructures. Using this method and quantum chemistry methods, the trigger properties of metal nanoclusters, proton and superionic conductors, superconducting systems, nanoporous crystals of the natural zeolite family were studied.

All research trends at the Novosibirsk Institute of Organic Chemistry (NIOC) are associated with the name of its founder, Academician N N Vorozhtsov, a prominent scientist in the chemistry and technology of aromatic compounds, organic intermediates and dyes. He and his followers developed the synthetic chemistry of aromatic compounds, a general approach to the preparation of polyfluorinated aromatic compounds starting from available polychlorinated analogues. One more line of research initiated by N N Vorozhtsov was concerned with the mechanisms of most important reactions of aromatic compounds and the structures and properties of carbocations. This subject was further developed in Academician V A Koptyug's studies. The series of studies dealing with carbocations carried out under his supervision was awarded in 1990 the Lenin prize, the most prestigious prize in the USSR. Since Siberian flora is a source of an enormous number of biologically active compounds, N N Vorozhtsov established the Laboratory of Natural Physiologically Active Compounds at the Institute. This research started by Professors V A Pentegova and V A Barkhash was successfully continued by Academician G A Tolstikov. Currently, target-directed synthesis of drugs and modification of plant metabolites form an important field of investigations carried out at the NIOC. In particular, Academician G A Tolstikov supervised the synthesis of new derivatives of betulonic acid, which was synthesised from betulin extracted from the birch bark. Many amides and peptides of betulonic acid are active inhibitors of tumour cell growth. Studies on transformation of readily available plant di- and triterpenoids and diterpene isoquinoline alkaloids aimed at the elaboration of promising antiviral, anaesthetic, cardiostimulating and antitumour drugs are carried out at the Institute.

The main field of research carried out at the Institute of Solid State Chemistry and Mechanochemistry (ISSCM) is related to solid-phase transformations. Academician V V Boldyrev and co-workers elucidated the influence of defects in a solid on the mechanism and the rate of solid-phase transformations. By selecting the methods for the production and pretreatment of solids, they succeeded in carrying out many solid-phase processes not only absolutely without wastes, but also with a considerable decrease in the number of stages and the time of the processing cycle. Among the most recent ISSCM studies, one can mention those of nanoparticle formation upon explosion carried out in cooperation with the G I Budker Institute of Nuclear Physics and the M A Lavrentiev Institute of Hydrodynamics of the SB RAS in the real-time mode using synchrotron radiation. These studies provided a deeper insight into the nature of fast processes and ensured the development of a number of explosion-based industrial processes, in particular, controlled synthesis of nanodiamonds.

The A E Favorsky Irkutsk Institute of Chemistry of the SB RAS (IrIC) is among the most prominent Russian centres for fundamental research in organic and organoelement chemistry. A leading Russian scientific school, which continues the tradition of the great Russian organic chemist A E Favorsky, has formed at the Institute. The research carried out at the Institute from the day it was founded has been mainly concerned with acetylene and complex organic and organoelement molecules synthesised based on acetylene. The chemistry of organic compounds of silicon with unusual valence represents yet another leading research trend of the Institute. Under the supervision of Academician

M G Voronkov, compounds with pentacoordinated silicon, the so-called silatranes, were prepared at the IrIC. Many new chemical reactions were discovered, the best known being the reaction of ketoximes with acetylene discovered by Academician B A Trofimov. This reaction gives rise to pyrroles, key fragments of important life-supporting metal complex systems (chlorophyll and haemoglobin) and has been included into monographs and handbooks as the Trofimov reaction. Numerous drugs, environmentally safe pesticides, plant growth regulators, polymers, fragrances, sorbents, complexones and metal and pollutant extractants, corrosion inhibitors, fuel and oil additives, new-generation materials for microelectronics and lithium batteries and energetic compounds for rocket propellants were developed at the Institute. Among new pharmacological agents prepared by Irkutsk chemists, mention should be made of Acyzole, which possesses antidote properties with respect to carbon monoxide, Cobazole, which actively stimulates haemogenesis, and Anavidin, a new-generation antiseptic and disinfectant. A new highly efficient antituberculosis agent Perchlozon active with respect to mycobacteria that are stable against standard antituberculous drugs is under clinical trials.

The setting of research of Siberian chemical institutes have always included a regional component. First of all, this implies systematic studies into the composition of diversified fossil and renewable raw materials and development of the methods for reasonable use of these resources, in particular, development of environmentally safe methods for their processing. The Institute of Chemistry and Chemical Technology of the SB RAS (ICCT) has accumulated highly valuable experience in the processing of plant biomass to produce various target products; in particular, methods for the production of microcrystalline cellulose from wood wastes were developed. The Institute contributed significantly to the development of the theory of structure of the surface and near-surface layers of minerals, in particular, those formed on sulfides in chemical and electrochemical reactions. On the basis of microscopic cenospheres present in the ash from carbon-based heat electric generation plants, microspherical zeolite sorbents, encapsulated inorganic ion-exchange materials and organic extractants for purification of liquid radioactive wastes of nuclear plants and waste waters of hydrometallurgical plants from radionuclides and nonferrous and noble metal ions were developed.

The Institute of Problems of Hydrocarbon Processing (recently, this was the Omsk Branch of the Institute of Catalysis of the SB RAS), together with the Institute of Catalysis were engaged in a highly important State innovation project in 2003 – 2006 and thus developed (and prepared for commercialisation) new catalysts for two important oil refining processes, namely, cracking and reforming; engine fuel production at Russian plants was successfully upgraded.

The Institute of Petroleum Chemistry of the SB RAS carries out extensive fundamental and applied studies directed at the creation of new science-intensive, environmentally safe, energy-saving processes for enhanced oil refining. Large-scale industrial use of these processes would extend the period of commercial production from fields at later stages of development and start the development of fields with oil reserves which are difficult to refine, in particular, with high-viscosity oils. The development and perfection of physicochemical, hydrodynamic, steam and microbiological methods for reservoir development and integrated processes that combine these ways of stimulation are in progress.

An essential contribution to the production of new highly energetic substances was made by one of the youngest Institutes of the SB RAS, the Institute for Problems of Chemical and Energetic Technologies, founded in 2001 by the Siberian Branch in close cooperation with the Federal State Unitary Enterprise 'Altay' in order to pursue the fundamental and applied studies in the development and use of energetic compounds, development of the methods of fine organic synthesis, and manufacture of new materials. An achievement of the Institute is the design of new high-enthalpy polymers and other components of rocket propellants with the record-breaking characteristics accomplished by Academician G V Sakovich.

When considering the chemistry-related studies carried out at the Siberian Branch of the RAS, it should be noted that they are far from being limited to the above-listed chemical institutes. For example, extensive advanced studies in bioorganic chemistry and physicochemical biology are carried out at the Institute of Chemical Biology and Fundamental Medicine (formerly, this was the Institute of Bioorganic Chemistry formed from a department of the Novosibirsk Institute of Organic Chemistry) and also in a number of other biological institutes.

The works on the design of new materials including nanomaterials and nanotechnologies are carried out at physical institutes. At some institutes of the SB RAS, research into the chemical essence of natural phenomena and objects is actively carried out (chemistry of atmosphere, geochemistry, *etc.*). Noteworthy are very promising studies of gas hydrates in permafrost zones and aquatic areas representing inexhaustible reserves of methane and physicochemical and analytical studies dealing with Baikal.

Finally, institutes of different disciplines make a great contribution to the development of new instruments and procedures and their adapting to the investigation of chemical processes and materials, as was mentioned above.

The principles of work of the Siberian Branch established by its founders allowed the Branch to survive during the hard years of perestroika and to adapt to work under market. The high level and the integrated character of fundamental research allow the Institutes to compete for, and win grants from, Russian and foreign funds and to award contracts with leading foreign companies. The system of training of scientific staff in the SB RAS ensures preservation of the scientific potential of the Branch at a high level, and the engineering design and pilot departments established at the institutes allow one to bring the scientific results to the level required for commercialisation, thus opening the way for new science-intensive industrial processes and attraction of investments. An important achievement of the SB RAS is the active functioning of world-level scientific schools. The works of scientists of the Branch have been repeatedly rewarded with prestigious prizes, prizes of the RF government and the Russian Academy of Sciences. Many scientists of the SB RAS are international prize winners, members of foreign Academies and international scientific associations.

This issue of the journal composed with significant participation of Professor V P Fedin includes reviews prepared by senior researchers of the chemical institutes of the SB RAS. Of course, this covers only a minor portion of results of studies carried out at these institutes. The subsequent issues of the journal would continue to acquaint the readers with the scientific results obtained by chemists of the Siberian Branch of the RAS.

Academician V N Parmon
Chairman of the Joint Academic Council
on Chemical Sciences of the SB RAS