“Green Chemistry in Russia” is a collection of scientific articles dealing with development of ‘Green/Sustainable Chemistry methods’ in former Soviet Union. Such techniques allow to design valuable chemical products minimizing damage to the environment.

Among the topics we can find: the utilization and processing of anthropic wastes (including particularly stable chlorinated aromatics), the purification of automotive exhausts from nitrogen oxides, the decontamination of water, the production of valuable materials from waste timber products, and the scientific classification and qualified use of humic substances.

This book is addressed to the specialists in the fields of ecology, chemistry, and sustainable development, to the high-school teachers and students, and to the post-graduate students, specializing in different fields of chemistry, chemical technology, and ecology.

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*Green Chemistry in Russia*

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*Green Chemistry Series n° 12*

# Green Chemistry in Russia

Editors:
Valery Lunin, Pietro Tundo, Ekaterina Lokteva

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in collaboration with IUPAC and INTAS

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**Green Chemistry in Russia**

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The editors are thankful to INTAS (International Association for the promotion of co-operation with scientists from the New Independent States of the former Soviet Union) for making this translation possible and for supporting worldwide distribution of this book.

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# INDICE

Introduction

# INTRODUCTION BY INCA

The field of green chemistry has received much attention from the scientific and industrial communities in almost every highly industrialized nation. It is understandable that the principles of green chemistry should generate strong interest in countries with high production capacities. One of these countries is Russia, which has a long history of chemical industry.

Unfortunately, that industry resulted in a number of highly contaminated sites and hazardous and resource consuming production tools. Industrial development in Russia took place during Soviet times, when there was no concern about environmental issues.

Although there was a decrease in production capacity in Russia in the two last decades, the country's scientific and technological potential remained valid. The renaissance of Russian industry, which has been observed for the last several years, has been based in part on the principles of sustainability. A particular focus on chemistry resulted in a nationwide effort by the research community (which has historically been the driving force for innovation) to invent, develop, and popularise new "green" chemical processes.

Even though not all the research directions to be reported in this book have found applications in industry, environmental protection, or elsewhere, the book will demonstrate that the ideology of green chemistry has never been hostile to Russian research and development. What is particularly important is that the book, which will be available in English, will share these innovations, for the first time with the foreign R&D community.

The book will deal with developments in the main regions of Russia: Central Russia, Northern Region, Siberia, Ural, and the Far East described in the book are the following:

- the nucleophilic aromatic substitution of hydrogen reactions that are ecological alternatives to the commonly used methods of introduction of substituents to organic molecules
- de-$NO_x$ reactions or $SO_2$ removal using new very effective catalysts containing transition metal cations
- new methods for transforming wood biomass to valuable products, based on examples from Siberian and Northern Russia woods
- new approaches to classification of humic substances and principles for using them for a number of chemical, agricultural, medical, and other purposes
- applications of ionic liquids for base-promoted reactions of CH-acids to obtain important agrochemical and medicinal products

The book will also address waste disposal and remediation problems and pollution control and monitoring. These issues are vital for Russia, where enormous amounts of PCBs are still stored and used in old electrical equipment.

This book was born by a joint collaboration between IUPAC (International Union of Pure and Applied Chemistry) and INCA (Interuniversity National Consortium "Chemistry for the Environment").

IUPAC is carrying out many activities related to Green Chemistry, most of them by its Subcommittee on Green Chemistry.

The aim of the IUPAC Subcommittee on Green Chemistry is to promote the cause of green chemistry for the wider benefit of the chemistry community and society as whole. For more information regarding the Subcommittee visit its Web site.

http://www.iupac.org/divisions/III/303/index.html

Among the projects already completed, it is noteworthy the Special Topic Issue on Green Chemistry published on Pure Appl. Chem. 2000, 72, 1207-1403.

http://www.iupac.org/publications/pac/2000/7207/index.html

An important current project is:

A IUPAC coordinated web page on Green/Sustainable Chemistry:

http://www.iupac.org/projects/2002/2002-029-1-300.html

INCA is a Consortium of 31 Italian Universities, which carries out research, education and promotes international collaboration in the wide field of Chemistry for the Environment. Web site: http://www.unive.it/inca/

In collaboration with IUPAC, INCA has already published:

Green Chemistry Education:

http://www.iupac.org/publications/books/author/tundo2.html

Green Chemistry in Africa:

http://www.iupac.org/publications/books/author/tundo.html

Next publications will be:

Green Chemistry in Latin America:

http://www.iupac.org/projects/2002/2002-064-1-300.html

Green Chemistry in the Arab Region:

http://www.iupac.org/projects/2003/2003-043-1-300.html

This book, “Green Chemistry in Russia” is the 12th publication of the INCA Green Chemistry Series. The previous ones are freely downloadable from the INCA web site and available upon request. See:

http://www.unive.it/inca/pubblicazioni.htm

I believe that the interesting and substantial material in this book will help many researchers, students, and people who are interested in the problems of environmental protection and safety, to obtain valuable information and perspectives on the development of green chemistry in Russia.

Pietro Tundo
University Ca’ Foscari of Venice
President of INCA
Chairman of the IUPAC Sub-Committee on Green Chemistry

# INTRODUCTION BY INTAS

INTAS is the International Association for the promotion of co-operation with scientists from the New Independent States of the former Soviet Union (NIS). Established in June 1993 as a European initiative, INTAS promotes scientific research activities in the NIS through an international effort; an essential element for social and economic progress in those countries. INTAS also encourages scientific co-operation between their scientists and the international scientific community through research projects and networks of scientific excellence. INTAS receives at present most of its financial support from the European Community, through the 6th Framework Programme, as a part of the “Specific Measures in support of international co-operation” (INCO), for the actions targeted towards Russia and the other NIS.

Environmental protection remains a major component of co-operative activities between Europe and the NIS. In particular, management of environmental risks associated with man-made changes, industrial, agricultural and military wastes, including risks for soil, water, air and the food chain and possible remediation are identified as one of the three priorities of the INCO program in the NIS. These are challenges that need to be faced worldwide. With that respect, Green Chemistry is a promising approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations. The concept of green chemistry was launched in the nineties, at the time the Soviet Union had just disappeared and its environmental legacy was revealed to the world. In Russia and other NIS inadequate environmental management has resulted in severe environmental pollution and contamination, leading to public health problems over large geographical areas. Well-known examples are oil contamination of vast territories; pollution of agricultural lands by pesticides and herbicides; contamination of soil and water by radioactive substances, and by heavy metals.

At the same time, the scientific community of Russia and other NIS was threatened of collapse because of a disastrous economical situation and uncontrolled transition to market-based economy. Yet NIS scientists had already gained great expertise in the monitoring of pollution and in the development of innovative techniques to address environmental problems. Their expertise should be used for further research in this direction, in order to significantly improve the environment and human habitat and, also, preserve biodiversity. No doubt that a better involvement of NIS scientific communities in pollution prevention and remediation is highly desirable, but this will happen only if major cooperation with the world scientific community will be attained.

Indeed, INTAS had recognized this situation and launched in 2001 a call for project proposals on Pollution. The call produced 20 projects, from “Novel calixarene ligands for the selective extraction of F-group elements from radioactive pollutants” to “The development of advanced bioremediation techniques for efficient treatment of industrial waste waters”. The editorial initiative “Green Chemistry in Russia”, born from the same concerns and aiming at the same results, is therefore fully in line not only with this INTAS call but also with INTAS strategic priorities. I am therefore very glad that INTAS is offered the opportunity to contribute to this very promising initiative.

Alain GERARD
Executive Secretary of INTAS

# INTRODUCTION BY MOSCOW STATE UNIVERSITY

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Environmental problems being faced by the humanity are of a global nature and inherent to all countries of the world. However, a lot of problems related to industrial pollution vary over individual countries and have their own specifics in Russia. This is mainly due to the high latitude of this country. Nowhere in the world industrial facilities can be encountered in regions where annual average temperature drops below 10°C. Instead half of the territory of Russia is situated in the permafrost zone and behind the Polar Circle. These areas are abundant in mineral resources: up to 42% and 13% of global reserves of gas and oil as wells as 40% of world nickel and platinum resources are concentrated in the Arctic Zone. Large metallurgic factories (Norilsk, Kola Peninsula), paper mills (Arkhangelsk paper-and-pulp complex), and other industries were built in these areas. Biological degradation of industrial wastes is extremely slow in the Arctic, yet northern wildlife is much more sensitive to their impact if compared to southern nature. That is why any blind adoption of western technologies along with proposed environmental risk assessments is often inapplicable for Russian conditions. In the days of the USSR, for resource saving, there used to be a widespread practice of building plants closely surrounded by residential areas close to water bodies, this dramatically increased human exposure to pollution. In addition to location there are other significant factors. It is worth mentioning that up to 40% of Russian industries are obsolete and inconsistent with environmental standards. Such standards just did not exist at the time of their designing and constructing. Anyway, even nowadays social factors, namely inadequate law enforcement by the government and general lack of respect to laws, hamper an environmental safety build-up in industries. As a rule, environmental issues occupy the bottom position in the list of their costs.

Therefore, training of specialists who would have a responsible attitude to our home country is a focal issue for Russia. If today’s students and postgraduates - chemists, chemical engineers - deeply realize that we do not and will never have another Earth, if they get to know the existing opportunities and already implemented developments in green chemistry, there is hope that they will further evolve this area of science and consecutively strive for minimization of environmental damage from operation of industrial enterprises. Hence, there would be a chance that our next generations will live under tolerable life conditions and be relatively healthy.

Lately, we fostered a shift from administrative methods, which prescribe end-of-pipe control of polluting emissions and destruction of hazardous substances, generated as a result of chemical processes, to their conceptual alternatives: green chemistry methods. When properly applied, green chemistry is a kind of art, which enables to not only prepare the target substances, but also, ideally, to do that in an environmentally safe way during each productive stage. Similarly to any perfectly assimilated motion that requires less effort for its implementation, the use of green chemistry methods leads to lower production costs, at least for the reason that no incineration or recycling stages are needed for the management of harmful by-products, since they are not generated at all. A decrease in the number of stages implies energy saving and positively impacts on environmental and economic assessments of a production site.

It is important to pinpoint that a “green chemistry” vision of research is likely to appear useful from the scientific standpoint. Such switch-over to another outlook often helps a scientist to view his own research in a new light and opens up new opportunities, what is beneficial for science as a whole.

From the chemist’s viewpoint, any improvement of chemical processes that have positive environmental impact may be assigned to green chemistry. P.T. Anastas and J.C. Warner in the book “Green Chemistry: Theory and Practice” [1] have formulated twelve green chemistry principles, which should be in mind of any researcher working in this field. They are listed below for the reader’s convenience.

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficiency of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc) should be made unnecessary wherever possible and, innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

It would be reasonable to split the issues within the competence of green chemistry into two areas. The first addresses recycling, reuse and destruction of environmentally hazardous side, and waste products in chemical and other industrial sectors in order to avoid environmental hazard or at least lower it to acceptable levels.

The other area, which is more attractive, deals with the development of new production processes that would operate absolutely without environmentally unsafe products (by-products included) or minimize their inputs and release. Production of caustic soda vividly illustrates how an alternative approach to production of one sole chemical product is able to entail a chain of positive environmental effects. This technology currently includes the electrolysis of sodium chloride in water solution:

$NaCl + H_2O + e\ (C, Hg, Ti) = NaOH + Cl_2$,
where “e” is the electrode, made of relevant material.

The reaction consumes much alkali and generates chlorine as a by-product. Researchers designed lots of technologies for chlorine industry to utilize this excessive chlorine. Meanwhile, there are chlorine-free alternatives for caustic soda production. Their scale-up will allow avoiding an excessive chlorine release and replacing chlorine-based chemicals for other, more environmentally-friendly products. For example, polyvinylchloride (PVC) is one of multi-tonnage commercial plastics, which is presently extensively used for consumer goods manufacture (windows, linoleum, toys, etc.). PVC possesses high consumer-oriented properties, i.e. it is durable, readily mouldable, and stable at ambient temperatures. At the same time, it bears potential risk as it incorporates up to 50% of chlorine. Hence, its recovery will be inevitably accompanied by a release of dioxins. PVC reuse is challenging and impedes recycling of other plastics, since PVC poorly mixes with them and cannot soften without degradation. Moreover, all three PVC production steps - ethylene chlorination to dichloroethane, dichloroethane dehydrochlorination to vinyl chloride and polymerization - generate dioxin emissions in stepwise growing amounts. In terms of a very wide scope of PVC applications, ultimate effects are likely to be extremely negative. This is why developed economies endeavour to move such productions to third countries. We can see everywhere around advertisements of plastic windows “from Germany”, which in fact have been manufactured for a long time here in Russia. At the same time, commercial technologies for production of metallocene catalysts have been recently developed. They are not so hazardous in terms of environment and are virtually capable of replacing PVC in all applications. If produced at a large scale, these polymers may be more cost-effective, although even today they are posing a threat for 15% of the PVC market.

This book largely focuses on technologies for management of hazardous organochlorine compounds or those produced in surplus amounts. This issue has been addressed in the researches carried out at N.D. Zelinsky Institute of Organic Chemistry RAS (headed by S.S. Yufit), A.N. Severtsev Institute of Environmental Problems RAS (headed by N.A. Kluev), G.K. Boreskov Institute of Catalysis RAS (headed by V.I. Simagina) and Department of Chemistry of M.V. Lomonosov Moscow State University. The material presented in the book provides a proper idea of what effort is needed for chlorine recycling and of how hard it is to select economically beneficial technologies that simultaneously would not be associated with environmental risks. In the meantime, application of chlorine-free alternatives will ‘nip this problem in the bud’. For instance, the paper by O.N. Chupakhin and V.N. Charushin (Institute of Organic Synthesis, RAS Ural Division) describes approaches to the replacement of halogen nucleophilic substitution in organic compounds for other functional groups by means of hydrogen nucleophilic substitution by the same groups. Numerous nucleophilic substitution reactions include a chlorination step, which is completely excluded in the proposed methodology. The paper gives a clear vision of future opportunities opened up by this reaction in the organic synthesis.

Industries frequently reject green chemistry principles on the basis of the idea that the proposed “revolutionary” industrial reforming is economically unjustified. In this case, optimal would be “evolutional” changes of production processes giving way to some improvement of environmental indicators on each production stage. Evolutional improvement of each production step of colour replenishers for stilbene-based detergents described in [2] can well illustrate the above. Acid concentration changing, organic solvent replacement for water, apparatus design modification, etc. allow a dramatic reduction of environmental damage from all production stages. Here, evolutional improvements, in our opinion, are fully realized in the light of green chemistry targets and methods and should not be opposed to them. Note that the fulfilled changes appeared to be economically beneficial as well.

Air pollution in Russian cities predominantly originates from two chemicals: nitrogen and sulphur dioxides. Naturally, there are other pollutants, some of them being even more hazardous, such as ammonia, benz-a-pyrene, etc. However, nitrogen and sulphur dioxides represent the majority of all industrial and urban traffic emissions in terms of quantity. Pollution from exhausts of motor vehicles is worth special mentioning: according to the World Health Organization data, up to 70% of diseases of adults and, especially, childhood pathologies are caused by these gaseous contaminants. Totally, up to 6.5 mln. t of nitrogen and 8.5 mln. t of sulphur were emitted in Russia in 1992. The specific geographical position of Russia is responsible for the fact that dominating winds transfer nitrogen and sulphur oxides from Ukraine, Germany, Poland, Belarus, Czechia, Slovakia, Finland and even UK to Russia. In turn, Russia "exports" to Europe emissions from Norilsk metal works and nickel smelter located on the Kola Peninsula. The metallurgic factories of Norilsk play a special role in heavy contamination of the northern regions of Russia. To this end, reduction of the $NO_x$ concentration in automobile exhausts and industrial air emissions remains a pressing objective. Two papers in this book address this issue: the one by V.F. Tretyakov and T.N. Burdeinaya – from A.V. Topchiev Institute of Petrochemical Synthesis RAS – and that by V.A. Sadykov and co-workers, who summarized research results of a team of Moscow and Siberian (Novosibirsk, Boreskov Institute of Catalysis) scientists.

Potable and waste water treatment is currently conducted by both physical and chemical methods. This collection of articles includes V.G. Sister's work on assessment of the ultrasonic impact potential for improving the water treatment parameters in electrocoagulation and flotation processes. The proposed method will enable to dramatically reduce consumption of reagents and raise water quality indicators: to improve clarity, to lessen heavy metals content, etc.

One paper deals with reclamation of natural environments. It is the article by I.V. Perminova et al. where the employment of humic substances for this purpose is discussed. It is one of the first sound attempts of scientific categorization of humic substances that allows systematization of their applications, most of which closely adjoin the green chemistry area.

The synthesis of new materials and purification of chemicals using supercritical fluids are among the green chemistry areas being developed in Russia. Supercritical carbon dioxide is in most frequent use; sometimes water, ammonia, propane, nitrogen and xenon are employed for the purpose. Carbon dioxide and water are environmentally-friendly and inexpensive reagents, therefore their use definitely complies with the targets and objectives of green chemistry. The key advantage of supercritical fluids is that they return to the Earth's atmosphere after a post-use pressure drop in the reactor. Moreover, there is no more need for large amounts of harmful organic solvents, which, usually, are utilized after the reaction for deep washing of the final products.

The substance properties change radically close to the critical point on the phase diagram. Water and $CO_2$ become effective solvents. Due to the inert nature of supercritical carbon dioxide, it is possible to carry out the synthesis of organic compounds in its media, including metal complexes, polymerization, as well as to extract desirable compounds with its help, e.g. salts of heavy metals from solutions. Moreover, it allows extraction from solids. For example, at the Institute of Radium (St. Petersburg) scientific grounds for extraction of transuranium elements – from radioactively polluted Chernobyl lands – were developed. In some polymerization processes, supercritical $CO_2$ dissolves fluorinated hydrocarbons. Dupont chose the technology based on this solvent for production of fluorinated polymers. The synthesis of other polymers is also achievable in the presence of perfluorocarbons. They prevent precipitation of the target polymer, e.g. polyacrylate, thanks to solubilization of the forming polymer molecule by surrounding perfluorinated groups; similarly to the action of surfactants which solubilize grease and dirt particles during washing. By the way, in Japan, supercritical $CO_2$ is already being extensively used in laundries and drycleaner's. Supercritical $CO_2$ is also actively utilized in other production sectors though mostly as an extraction agent. Only a few production technologies use it as a solvent in chemical reactions. Among the pioneers are the scientists from Nottingham University in UK who, jointly with Thomas Swan & Co. Ltd., during a short period managed to scale up the process of isophorone selective hydrogenation to trimethylcyclohexanone in the presence of a palladium catalyst to 1000 t/year [3]. The reactor was designed in a way that facilitates switching to new processes.

Researches focused on the use of supercritical $CO_2$ are being actively carried out in Russia - in MSU, INEOS (Nesmeyanov Institute of Organoelement Compounds RAS where they are headed by A.R. Khokhlov) and other research laboratories.

The use of water close to the critical point is more sophisticated and costly than that of carbon dioxide because of much higher critical temperature and pressures (374ºC, 220 atm.). However, the results may appear exciting as water acquires properties of an extremely strong solvent.

At the same time, it is necessary to take into account energy inputs needed to transfer a substance to the supercritical state. Environmental benefits from supercritical fluid applications should exceed environmental damage resulting from additional energy generation.

This book includes a paper discussing a research done at Severtsov Institute of Problems of Ecology and Evolution RAS. It shows supercritical water potentialities for the disposal of heavy polychlorinated persistent organic pollutants.

Development of new solvents for chemistry has not been limited by the use of supercritical fluids. An important area of green chemistry is the utilization of ionic liquids for routine organic chemistry reactions. Ionic liquids are non-volatile, non-inflammable, and – by varying their cations and anions – it is possible to design a solvent that would be perfectly tailored for its specific application. Russian researches in this area are presented by the work of S.G. Zlotin et al. from Zelinsky Institute of Organic Chemistry RAS.

The application of biological catalysts should be mentioned among the chemical processes modified according to principles of green chemistry. In the early 1990s, a biocatalytic process for acrylamide production was introduced in Russia (Perm). Its authors received the RF Government Award for this work in 1995.

Catalytic reactions make up a significant part of green chemistry processes. Indeed, a catalyst is used in small amounts and usually can be regenerated. At the same time, it often considerably improves productivity and selectivity of the process. For instance, recently there has been a tendency to perform nitration of aromatic compounds using nitric acid alone rather than its mixture with sulphuric acid, this diminishes environmental risks. Certain sorts of zeolites speed up the process and contribute to its selectivity if used as catalysts. Zeolites – natural and synthetic clays – are quite environmentally safe, can be readily separated from the reaction medium and regenerated by the azeotropic water removal. A relatively new area of catalyst applications is the synthesis of biodegradable polymers to be used instead of available persistent types. A catalytic process made it possible to lower the temperature of the polyaspartic acid preparation and improve its physico-chemical characteristics. This polymer may replace polyacrylic acid that does not degrade in nature. Additionally, it is potentially usable as a corrosion and deposit inhibitor in water treatment systems. In future, catalytic processes will allow creation of new materials (including polymers), which will not need additives, plasticizers, combustion inhibitors, etc., i.e. chemicals that prevent reuse of materials.

One of the ways for achieving the green chemistry goals is synthesizing chemical products from natural compounds. The preparation of alcohol from grain is a typical green chemistry process. As this process is cheaper than production of alcohol by ethylene oxidation, the latter has been terminated actually worldwide. Today’s cost of grain alcohol is about 300 USD per ton (versus 600 USD/t for ethylene-based alcohol produced by the classical scheme), but if biotechnological alcohol becomes twice cheaper it is likely to be a source for ethylene and polyethylene fabrication. In future, this will give way to almost a complete refuse from oil as a key feedstock of chemical industry and switch to renewable sources of raw materials. To this end, it is critical for Russia to keep pace with the most developed countries in such researches. Our current welfare is largely oil-dependent, yet reserves of oil are not infinite and its cost keeps on growing in relation with its production conditions (Arctic shelves, permafrost, swamps). For this reason, provided there are notable advances in biotechnologies, western customers may discontinue their use of oil. This situation will radically modify the structure of production sectors and Russia should be ready for that.

A main feedstock for this area of green chemistry is the vegetable biomass, to be exact, lignocellulose and starch. Available methods of lignocellulose recycling have not been sufficiently developed so far, yet, as the bulk of agricultural and domestic wastes consists of lignocellulose and cellulose, their transformation to sugars would incredibly speed up the progress in the field of environmentally safe technologies for chemical production. This book includes articles by K.G. Bogolitsyn et al. (Arkhangelsk State University of Technology) and B.N. Kuznetsov et al. (Institute of Chemistry and Chemical Technology, RAS Siberian Division, and Krasnoyarsk State University), which focus on a deep examination of the structure and chemical properties of lignins. These researches are definitely an essential step towards successful technologies of lignin transformation into sugars. Thus further solutions are clear: e.g. using enzymes, sugars will be transformed into organic acids (citric, lactic, oxalic acids, etc.) and those acids will serve as a raw material for a great number of other chemical products. In particular, dehydration of lactic acid will let achieve acrylic acid. Using such acid, it will be possible to synthesize acetaldehyde, ethylene glycol, tetrahydrofuran, propane diol, etc. Besides, organic acids themselves are valuable chemicals. Polylactate – a polymer prepared on the basis of lactic acid – is a good polyethylene and polypropylene substitute in packing films: it is nontoxic and, at the same time, readily degradable in nature (literally, over a few weeks). It is important that the vegetable feedstock does not bring about additional $CO_2$ emissions to the environment: carbon dioxide will ultimately emit in the same amount that was spent on the biomass formation in the course of the photosynthesis.

We hope that the material presented in this book will help young researchers and scientists who were brought up on the classical chemistry principles to understand the state of the art in the field of green chemistry researches in Russia and their outlook for the future as well as it will stimulate their interest for a job in this key sector of modern chemical science.

Finally, we would to address our special thanks to the International Union of Pure and Applied Chemistry (IUPAC) and to the Italian Interuniversity Consortium “Chimica per l’Ambiente” (“Chemistry for the Environment”; INCA) for the funds provided for the realization of this project. We also highly appreciate financial support of INTAS in the form of a grant for the translation of this book into English.

1. P. Tundo, P. Anastas, D. StC. Black, J. Breen, T. Collins, S. Memoli, J. Miyamoto, M. Poolyakoff, and W. Tumas: Synthetic pathways and processes in green chemistry. Introductory overview, Pure Appl. Chem., 2000, Vol. 72, No. 7, 1207-1228.
2. P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998, p. 30
3. S .Cook. Green chemistry – Evolution or Revolution? Green Chemistry, Oct. 1999, G138-G140.
4. P. Licence, J. Ke, M. Sokolova, S. K. Ross, M. Poliakoff. Chemical reactions in supercritical carbon dioxide: from laboratory to commercial plant. Green Chemistry, 2003, 5, pp. 99–104
5. S.S. Yufit. Toxins around us. – M.: James , 2001, 400 p.
6. L. Viktorov. Green chemistry wins. Chemistry and Life, 2001, _ 12 (in Russian).
7. S.M. Komarov. Cuvette with a supercritical fluid. Chemistry and Life, 2000, _2. (in Russian)
8. S.D. Varfolomeev, V.I. Lozinsky, E.I. Rainina. Cryoimmobolized enzymes and cells in the organic synthesis. Journal of Pure and Applied Chemistry, 1992, v.64, No. 8.
9. P.T. Anastas, M.M. Kirshhoff, T.C. Williamson. Catalysis as a foundational pillar of green chemistry. Applied Catalysis A: General, 221, v.2001, pp.3-13.

# $S_N^H$ REACTIONS: ASPECTS OF CREATION OF NEW ENVIRONMENTALLY ACCEPTABLE TECHNOLOGIES

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Today, the fact that quality of life is largely dependent on the level of chemical technology sophistication and supported by the use of polymeric engineering and constructional materials, synthetic textiles, dyes, medicines and a wide diversity of other chemical products (fertilizers, pesticides and insecticides, household chemical goods, etc.) hardly needs any proof. At the same time, a growth of chemical production has led to a tremendous build-up of tailings and horrifying sumps around chemical plants as well as smoke and adverse odours accompanying chemical production.

The research for new technologies minimizing the anthropic impact on the environment is currently an issue, pressing as never before. For this reason, not only economic effectiveness, but also environmental tolerability are becoming the key criteria for selection of technological solutions.

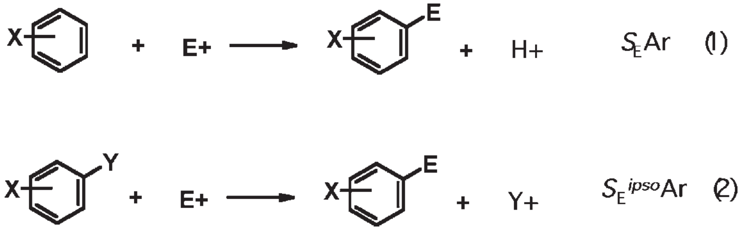
One of the rational approaches implies that, among the existing technologies, some engineering techniques and methods are dedicated to resource-saving: reduction of energy inputs through heat recovery, close-loop schemes for water use, waste recycling, etc. A more radical direction of this vital activity is design of new chemical processes that would allow to decrease energy consumption, to reduce the amount and, ideally, to absolutely avoid generation of by-products that need landfilling. Great future here definitely belongs to the catalysis and new reaction types, which will allow evading involvement of compounds containing halogen, sulphur, mercury, lead, and cadmium atoms and other potential sources of ecotoxicants in chemical processes. In international literature such processes are commonly named “environmentally-friendly reactions”.

Among the possible routes leading to the reduction of the environmental impact and to resource-saving are reactions involving *nucleophilic aromatic substitution of hydrogen* ($S_N^H$ reactions), They should be considered as a counterweight to substitutions of readily leaving groups, mainly chlorine, which are currently widespread in aromatics chemistry in spite of their imperfection. The ability of chlorine atoms to be substituted by amino, hydroxy, alkoxy and other groups in the aromatic ring under the action of nucleophiles has been widely used in the industrial organic synthesis for many decades. Today, these methods, having already become traditional, do not meet the requirements of modern environmental quality standards. This served as an incentive for starting up an international program focused on creation of chlorine-free chemical processes and products [1].

The first baseline review on $S_N^H$ reactions appeared in Russian literature more than 25 years ago [2], it was an innovative publication at international level as well. Regretfully, the book “Nucleophilic Aromatic Substitution of Hydrogen” [3], published in the USA in 1994 is next to being unavailable in Russia. To this end, it seems reasonable to give chemists engaged in aromatics chemistry at least a brief idea of basic theory and practice of $S_N^H$ processes, which were partially already implemented in industry.

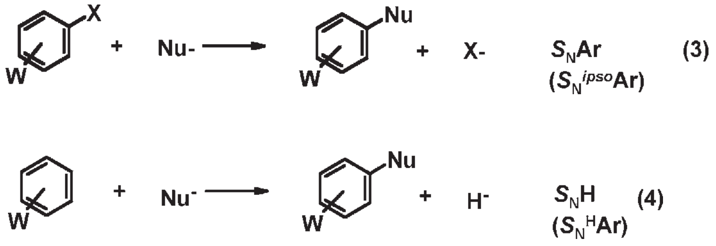
Aromatic compounds comprise about one third of all organics. It is hard to overestimate their role in production and development of new materials, polymers, dyes, pharmaceuticals, pesticides, food additives, etc.

Basic techniques of aromatic raw material functionalization are reactions of electrophilic ($S_EAr$) and nucleophilic ($S_NAr$) substitution. The majority of $S_EAr$ reactions refer to substitution of a hydrogen atom, while the so-called ipso-substitution, i.e. displacement of non-hydrogen particles (e.g. COOR, $NO_2$, $NR_2$, etc.) are of much rarer occurrence.



**Y= COOR, $NO_2$, $NR_2$ etc.**

Alternatively, quite recently ipso-substitutions ($S_N^{ipso}Ar$) used to be the most popular type of nucleophilic aromatic substitutions and hydrogen substitution reactions ($S_N^HAr$) were much less common.



**W – electron acceptor group**
**Y – leaving group**

If we strictly follow Ingold's classification, $S_NAr$ should be denoted as $S_N^{ipso}Ar$ and $S_EAr$ transformations as $S_E^HAr$. Modern literature more often uses symbols $S_EAr$, $S_NAr$, $S_E^{ipso}$, and $S_N^H$. In the two latter cases, the symbol Ar is omitted, as these reaction types primarily refer to aromatics.

A bibliography review shows that educational literature has been historically featuring a certain disproportion in describing both electrophilic and nucleophilic substitution reactions. Whether large sections of textbooks are devoted to the former reactions – discussing their synthetic opportunities, orientation effects, mechanisms, etc. – the latter are generally scarcely covered. Monographic literature on $S_N$Ar transformations is also by far scanty if compared to $S_E$Ar, although this is beyond any explanation, since both types of reactions occupy rather equal positions in today's chemical technology [4].

The interpretation of $S_N^H$ reactions deserves special attention. They are either completely missing in textbooks or merely mentioned in combination with comments such as "…reactions of nucleophilic substitution of hydrogen in the benzene nucleus are low probable…". In the absence of a generic conception, these transformations were described in publications as "uncommon" or "surprising" phenomena.

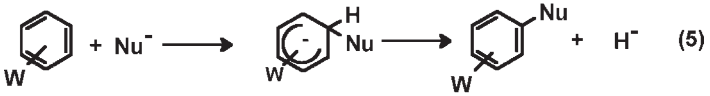
In this paper, we would like to show that $S_N^H$ transformations are not something exotic or surprising. On the contrary, they are amongst the fundamental properties of arenes (heteroarenes). By now, huge material has been accumulated to demonstrate their high synthetic potentialities that allow building of $C_{arom.}$-C, $C_{arom.}$-Hal, $C_{arom.}$-N, $C_{arom..}$-O, $C_{arom.}$-P, and $C_{arom.}$-S bonds under mild conditions. Some of the $S_N^H$ reactions entered the manufacturing technology pool long ago (synthesis of nitrophenol, alizarin, 2-aminopyridine), the other are among the most advanced industrial methods [5].

Stringent requirements to environmental safety of productions justify the promising future of commercial application of the discussed reactions. Indeed, to implement the $SN^{ipso}$Ar process it is necessary, first, to introduce groups, such as Cl, $NO_2$, $SO_3H$, etc., into the aromatic nucleus singularly for their further removal; then focus on waste disposal. Reactions of the $S_N^H$ type do not demand preliminary functionalization of a π-deficient aromatic (hereoaromatic) compound and the leaving group formally is a hydride ion. In reality, it means a removal of water from the reaction mass in a large group of transformations – this hardly needs any comments.

There exist main types of nucleophilic aromatic substitutions of hydrogen differing in the reaction mechanism: $S_N^H$(AE), $S_N^H$(EA) and $S_N^H$(ANRORC). This publication discusses only the first reaction type.

## $S_N^H$ (AE) REACTIONS

This transformation type is the most widespread one. The abbreviation $S_N^H$ (AE) reads: nucleophilic substitution of hydrogen by a mechanism "addition-elimination" characterized by a common specific feature – a two-step mechanism, at first, with the formation of an intermediate $\sigma^H$-adduct resulting from nucleophile addition to π-deficient arene (heteroarene), followed by hydrogen elimination formally as a hydride ion (Scheme 5).



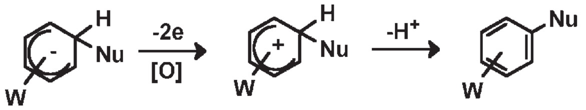
(5)

As seen from Schemes 3 and 4, $S_N^H$ (AE) reactions have common features with $S_N^{ipso}$Ar reactions. At the same time, there are significant distinctions. In the majority of cases, $\sigma^H$-adducts are more stable than their $\sigma^X$-analogs, the so-called Meisenheimer complexes.

The main reason for higher stability of $\sigma^H$-adducts lies in the nature of leaving groups. Opposite to “good” leaving groups being easily solvated in the form of anions $X^-$ (Scheme 3), e.g. Hal, CN, $NO_2$, $SO_3H$, etc., the hydride ion is not inclined to solvation and we failed to detect it as a kinetically independent particle in solutions. The occurrence of hydrogen either in the $H^+$ or $H^\bullet$ form is much more favourable thermodynamically than as $H^-$. Therefore $\sigma^H$-adducts are mainly not directly aromatized, but they are either through oxidation or the so-called “autoaromatization”.

Oxidative aromatization is a variation of $S_N^H$ (AE) reactions where the elimination step occurs as a redox process. In this sense, this reaction species may be designated as $S_N^H$ (AO) - nucleophilic substitution of hydrogen by a scheme “addition-oxidation”. Here, the $\sigma^H$-adduct loses two electrons and a proton (or one electron and hydrogen atom), what in total is equivalent to elimination of the hydride ion.

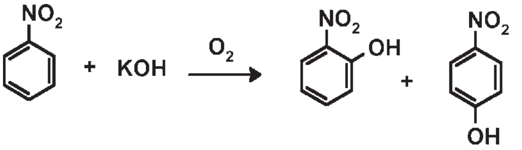
A simplified scheme of oxidative aromatization is likely to have the following view:



(6)

Thus, the oxidant changes the state of hydride-active hydrogen, which is ultimately eliminated as a proton: $H^- = 2e + H^+$.

The application of air oxygen as an oxidant is a well-known technique for carrying out $S_N^H$ reactions. A good example is the synthesis of nitrophenols proposed more than one hundred years ago (Scheme 7).



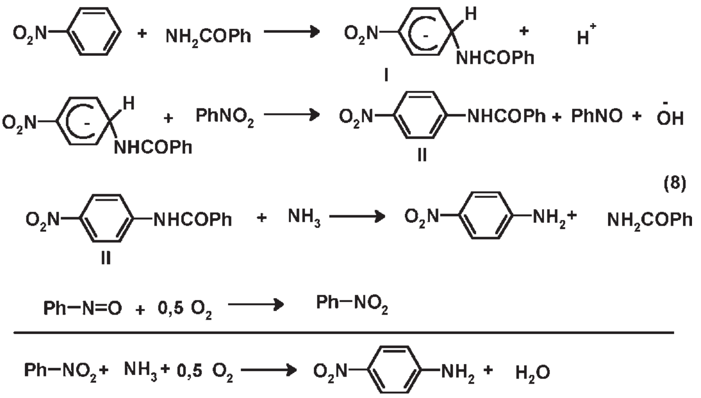
(7)

Numerous diverse aromatic and heteroaromatic compounds have been successfully functionalized by direct nucleophilic amination, halogenation, hydroxylation, alkylation, cyanidation, arylation, thiolation, phosphorylation, and other $S_N^H$ reactions, using oxidizing agents. The latter comprise both inorganic – halogens, hypohalogenites, potassium permanganate, sulfur, oxygen, metal cations, etc. – and organic reagents like triarylmethyl and tropylium cations, quinines and their derivatives, N-bromosuccinimide, heterocyclic cations and other compounds. Electrochemical oxidation of intermediates is also possible.

In the absence of an oxidant, its function can be fulfilled by the initial π-deficient arene (heteroarene). It is capable of implementing dehydrogenation of the $\sigma^H$-adduct and its transformation to the end product. In this process, the initial substance undergoes different levels of reduction and yields a by-product. Such type of dehydrogenation was given the name [6] of "spontaneous" aromatization.

An excellent, even exemplary, illustration of a waste-free $S_N^H$ technology is the 4-nitroaniline synthesis from nitrobenzene and benzamide that combines spontaneous aromatization with simultaneous participation of air oxygen [5].

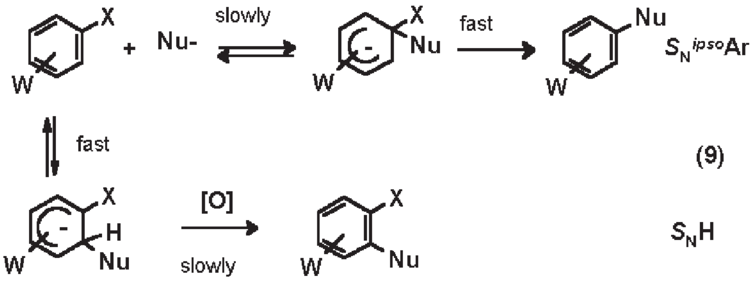
$\sigma^H$-Adduct I formed on the first step undergoes spontaneous oxidation by initial nitrobenzene, it transforms to product II via hydrogen substitution of the residual benzamide becoming nitrobenzene, which in its turn reduces to nitrosobenzene. Then the ammonolysis of compound II is conducted where desirable 4-nitroaniline is generated along with benzamide, which is returned to the first reaction step. As for nitrosobenzene, air oxygen oxidizes it to nitrobenzene. Summation of the equations (8) leads to the conclusion that 4-nitroaniline is synthesized actually from nitrobenzene, ammonia and air oxygen. The by-product is water.



An oxidizing agent plays a decisive role in a number of cases. The reversibility of the addition step may cause the $\sigma^H$-adducts yield in a failing low stationary concentration, and then the end product can be achieved only with participation of an oxidant.

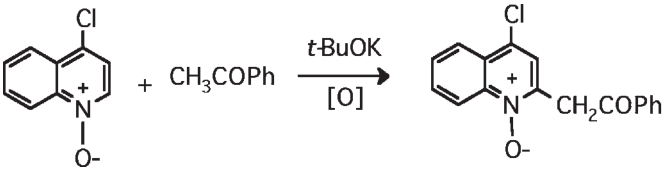
When using an oxidant, we have to remind that the oxidation process may affect the nucleophile, though, in the majority of cases, that does not obstacle realization of $S_N^H$ reactions. Omitting the details, it is possible to state that the employment of an oxidant frequently leads to high, close to quantitative, yields. Amination of azines by liquid ammonia in the presence of potassium permanganate [3] can serve as a model illustration for these reactions.

A critical implication is that $\sigma^H$-adducts are always registered as a kinetically regulated intermediate, i.e. carbon atoms carrying hydrogen rather than X are attacked first. Thereby a chance for obtaining $S_N^H$ products is the use of an oxidant and readily leaving groups retained in the substrate. Groupings X can be involved in further functionalization of arene (heteroarene).



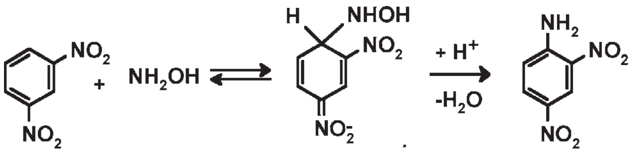
(9)

Scheme (10) illustrates the interaction of quinoline 4-chloro-N-oxide and the acetophenone anion with the preservation of chlorine, which is highly inclined to nucleophilic substitution in the reaction product.



(10)

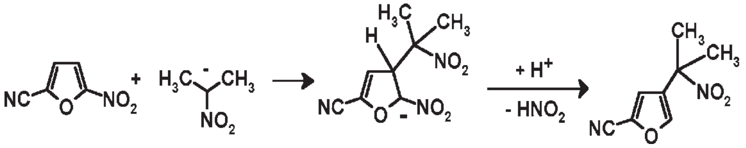
Autoaromatization. The presence of an auxiliary group plays the key role in autoaromatization processes. If the intermediate $S_N^H$ adduct incorporates an auxiliary nucleofug group A (Scheme 16), the electron density redistribution in the $\sigma^H$-adduct proceeds in such a way that the group A may split off in the form of an anion and this allows hydrogen elimination in the form of a proton. A well-known example of a $S_N^H$ reaction with autoaromatization is dinitrobenzene amination by hydroxylamine described long time ago (Scheme 11).



(11)

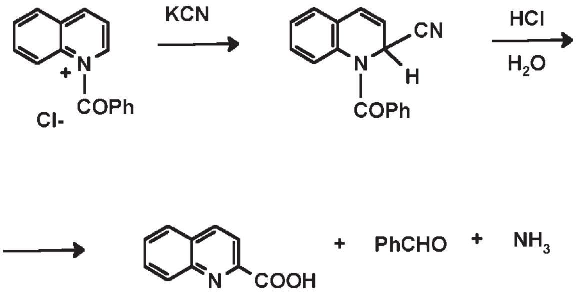
Several hydrogen aromatization options are feasible depending on a relative position of the substituted hydrogen atom and auxiliary group A.

If the group A is *ortho*-positioned toward the attacked carbon atom inside the nucleus, such reactions are considered as *kine*-substitutions. An example of *kine*-substitution is the reaction of 2-nitro-5-cyanofuran with the 2-nitropropane carbanion (12). Here, hydrogen is substituted in position 3 of the furan ring, with the nitro group simultaneously leaving position 2.



(12)

Reactions of N-oxides and their derivatives with nucleophiles should be assigned to kine-substitutions. In these reactions, at the aromatization step, N-oxide, N-alkoxide and N-acyloxide function as auxiliary groups A in elimination of hydrogen from the intermediate, e.g. Reissert reaction:

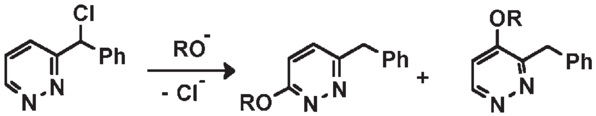


(13)

The scheme (13) shows that, along with the target carboxylic acid, the reaction yields aldehyde, which is a molecule of special interest (by the way, Reissert reaction is sometimes used to prepare aldehydes).

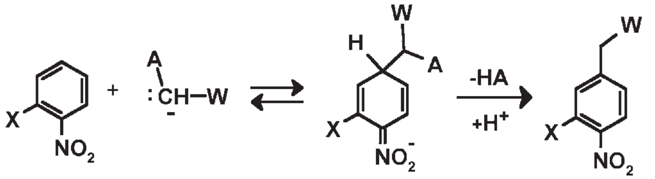
When there is one (or more atoms) positioned between the nucleophilic attack site and group A in the nucleus, it is *tele*-substitution. Below is given an example of this reaction with participation of 8-bromo-1,7-naphthiridine. NMR analysis proves that the reaction proceeds through the formation of a $\sigma^H$-adduct, which is then aromatized with the help of the *tele*-positioned bromine atom, evidently by 1,4-elimination of HBr.

*Tele*-substitutions have been registered for arenes containing the auxiliary group not in the nucleus but in the side chain.



(15)

A special and well-studied type [7] of autoaromatization is the so-called “vicarious” nucleophilic substitution where an auxiliary (vicarious) group (most often a halogen) is present not in the substrate but in the reagent, at the carbon atom, which is the C-nucleophile reaction centre. The attack of arene by the carbanion in the $\sigma^H$-adduct brings about a structural situation (16) that allows β-elimination of HA (as a rule, HHal).

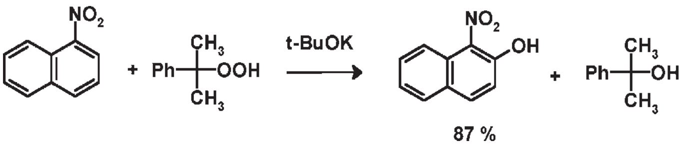


(16)

**A - auxiliary nucleophilic grouping (Cl, CN, OAr, SAr)**
**X - nucleofug group (Hal, CN, $SO_3H$, NO2, etc.)**
**W - electron acceptor remainder ($SO_2Ph$, SPh, CN)**

In the strict sense, all the discussed cases of autoaromatization (Schemes 11-16) are vicarious, i.e. it is indirect nucleophilic substitution of hydrogen, because a split-off of the hydrogen particle becomes possible with the aid of other atoms or groups present in the $\sigma^H$-adduct’s structure and capable of anionic stabilization. This also pertains to *kine*- and *tele*-substitutions, reactions of N-oxides and other similar transformations. However, the term "vicarious" is used in literature for the reactions of type (16).

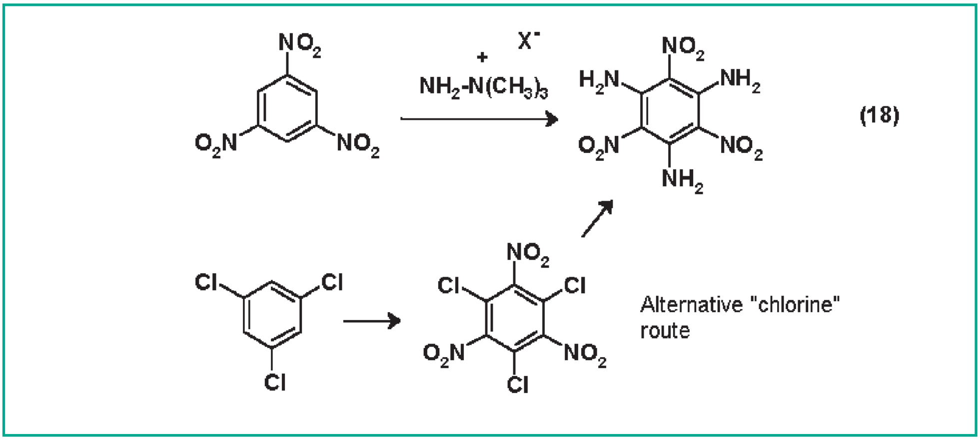
Vicarious nucleophilic substitutions pave the way to rather wide synthetic opportunities. They are used not merely for the nitroarene series, but also for heteroaromatic compounds, π-complexes of arenes, non-benzoid systems, etc. Examples of vicarious $S_N^H$ reactions, definitely commercially attractive, are interactions of nitroarenes with relatively stable and available tert-butyl and cumyl peroxides. This methodology is a general and simple synthetic route to nitrophenols and nitronaphthols; it is easily practicable for operations with large amounts of reagents [7]. Note that phenols are prepared without preliminary introduction of a sulfo group or halogen into nitroarene and the reactions proceed under mild conditions.



(17)

Alcohols generated as by-products can be easily separated and utilized.

Another striking example of using the concept of $S_N^H$ reactions may be the industrial synthesis of triaminotrinitrobenzene by direct amination of trinitrobenzene with 1,1,1-trimethyl-hydrazinium hydrosulfate as a vicarious agent. This alternative has been successfully competing with the environment-unsafe "chlorine" process with participation of 1,3,5-trichlorobenzene (Scheme 18) and actually pushing it out.



## CONCLUSION

We have discussed the grounds of modern understandings about $S_N^H$ reactions. Quite recently they used to be associated with Chichibabin reaction, hydroxylation of nitrobenzene, synthesis of alizarin, i.e. with the processes occurring under stringent conditions, what is natural in terms of the high-energy nature of the displaced $H^-$ particle. This situation did not stimulate chemists to investigate this area. This pattern entirely changed today. Modern data on the reaction mechanism give a clear idea of a necessity to fulfil an indirect removal of the hydride ion. This knowledge has undeniably contributed much to the progress in this field of research through development of diverse and convenient synthetic methods with the use of $S_N^H$ reactions.

The cited examples and the increasing number of publications related to this subject do not leave doubts about $S_N^H$ reactions being "…one of the most exciting and successfully advancing areas of organic chemistry" [6] with high opportunities of devising environmentally acceptable technologies.

## REFERENCES

1. Yufit S.S. "PVC - Chlorine Cylinder", M., Publishers "Dva Mira", 1998, p.26 (in Russian).
2. Chupakhin O.N., Postovsky I.Ya., *Advances of Chemistry*, 1976, v.45, p.908 (in Russian).
3. Chupakhin O.N., Charushin V.N., van der Plas H.C. "Nucleophilic Aromatic Substitution of Hydrogen". San Diego, N.Y., Academic Press 1994. 367 p.
4. Gorelik M.V., Efros L.S. "Essentials of Aromatics Chemistry and Technology", Khimia, M., 1992. 640 p. (in Russian).
5. Stern M.K., Baskin K.J., US Patent 5 117063 (1992).

6. Terrier F. “Nucleophilic Aromatic Displacement”. Weinheim, VCH. 1991. 375 p.
7. Makosza M. Izv. RAN, ser. Khim., 1996. 3, p.531-544 (in Russian).

# REACTIONS OF CH-ACIDS AND POLYCHLORINATED ORGANIC COMPOUNDS IN IONIC LIQUIDS

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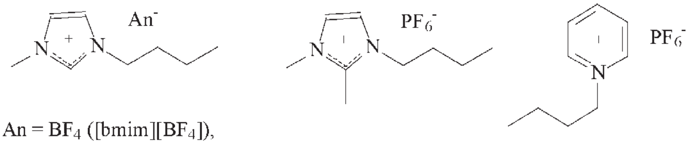
Organic solvents are environmental pollutants that evaporate to the atmosphere and then migrate to water bodies due to their volatility and uncontrolled emissions. A lot of solvents are toxic and produce adverse impact on the biosphere. In a number of cases, the use of molecular solvents does not ensure the desired selectivity of chemical processes. During last years, many countries feature a growing tendency of intensifying investigations focused on exploring alternative solvents for chemical research and industrial applications. Room-temperature liquid salts of inorganic and organic acids with bulky organic bases (so-called "ionic liquids") constitute an important part of these researches. Whereas in 1999 only 58 papers and patents were devoted to ionic liquids, in 2000 the number of relevant publications reached 134, in 2001 - 350 and in 2002 - more than 550 [1]. Ionic liquids, as a rule, are stable, nonvolatile and non-inflammable; they readily dissolve a large range of inorganic, organic, organometal compounds, and gases. They can be regenerated and reused [2]. At present, they show great potential as solvents and catalysts for chemical [3,4], biochemical [5], and electrochemical [6] processes, including separation of rare and dispersed elements [7], preparation of nanomaterials [8], membranes [9], and other technologies [10].

Ionic liquids used as reaction media yield valid - and so far unexplored - opportunities for the synthesis of fine organic chemicals. By selecting a proper cation-anion combination, they allow a wide-range regulation of the ionic solvent parameters, i.e. polarity, dissolving capacity, nucleophilic and electrophilic properties, thereby affecting the reaction direction, depth and selectivity [1].

We took advantage of the high polarity [11] and complexing capacity [12] of ionic liquids for carrying out liquid-phase chemical processes, including reactions accompanied by the carbon-carbon bond formation and carbon-halogen bond split. Base-promoted reactions of CH-acids with electrophiles found wide applications in the organic synthesis of complex polyfunctional molecules, e.g. biologically active substances [13]. The use of ionic liquids as a reaction media for the destruction of toxic organic congeners (polychlorinated hydrocarbons, dioxins, pesticides, etc.) appears practicable. The low volatility and the possible recycling of a solvent in such processes dramatically minimize the environment pollution risk. In this article we have examined reactions of CH-acids and polychlorinated organic compounds in ionic liquids of the imidazole and pyridine series. The ionic solvent was each time tailored for the individual reaction by changing the anion (Scheme 1).



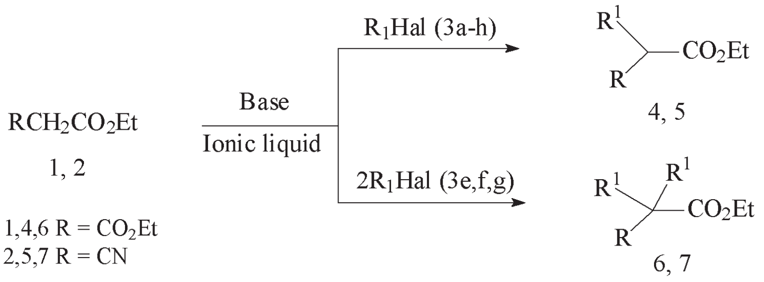
An = $BF_4$ ([bmim][$BF_4$]),
$PF_6$ ([bmim][$PF_6$]),
Br ([bmim][Br])

[bdmim][$PF_6$]

[bpy][$PF_6$]

**Scheme 1. The examined ionic liquids.**

We have developed a new approach to conducting CH-acid alkylation reactions based on the utilization of ionic liquids as reaction media. Malonic (1) and cyanoacetic (2) esters react with alkyl, benzyl and prenyl halogenides (3) in the ionic liquid in the presence of alkali metal hydroxides and carbonates yielding C-alkylation products (4 and 5) in 53 - 80% of cases. When an excess of the alkylating agent is used, double-alkylation products (6 and 7) are generated (Scheme 2) [14 a,b].

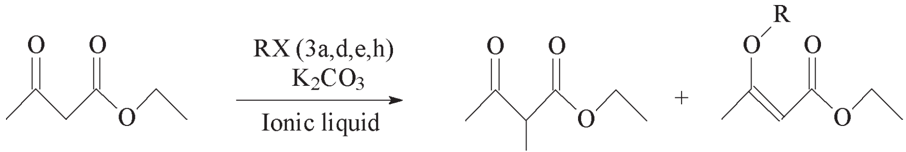


| No. | R | R1 | Hal | Base | Ionic liquid | Time, h | Temp., °C | Yield, % |
|---|---|---|---|---|---|---|---|---|
| 4a | $CO_2Et$ | $Bu^n$ | Br | $K_2CO_3$ | [bmim] $[PF_6]$ | 12 | 90 | 80 |
| 4b | -"- | $Pr^i$ | Br | $K_2CO_3$ | -"- | 20 | 90 | 54 |
| 4c | -"- | $C_5H_9c$ | Br | $K_2CO_3$ | -"- | 15 | 120 | 57 |
| 4d | -"- | $C_5H_{11}{}^i$ | Br | $K_2CO_3$ | -"- | 15 | 120 | 70 |
| 4e | -"- | $PhCH_2$ | Cl | $K_2CO_3$ | -"- | 5 | 120 | 72 |
| 4g | -"- | $(CH_3)_2C=CHCH_2$ | Cl | $K_2CO_3$ | -"- | 5 | 90 | 53 |
| 4h | -"- | Ger [a] | Cl | $LiOH/H_2O$ | -"- | 2 | 20 | 62 |
| 5a | CN | $Bu^n$ | Br | $K_2CO_3$ | [bmim] $[BF_4]$ | 18 | 60 | 76 |
| 5f | -"- | $CH_2=CHCH_2$ | Br | $K_2CO_3$ | -"- | 12 | 15 | 82 |
| 5g | -"- | $(CH_3)_2C=CHCH_2$ | Br | $LiOH/H_2O$ | -"- | 10 | 15 | 53 |
| 5h | -"- | Ger [a] | Cl | $LiOH/H_2O$ | [bmim] $[PF_6]$ | 3 | 35 | 54 |
| 6e | $CO_2Et$ | $PhCH_2$ | Cl | $K_2CO_3$ | -"- | 7 | 120 | 64 |
| 7f | CN | $CH_2=CHCH_2$ | Br | LiOH/H2O | [bmim] $[BF_4]$ | 24 | 20 | 80 |
| 7g | -"- | $(CH_3)_2C=CHCH_2$ | Br | $LiOH/H_2O$ | -"- | 5 | 20 | 60 |

[a] **Ger = $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_2$**

**Scheme 2. Alkylation of malonic (1) and cyanoacetic (2) esters promoted by bases in ionic liquids.**

The ambident anion of acetoacetic ester exhibits dual reactivity under the reaction conditions, yielding - along with the C-alkylation products (9) - relevant vinyl ethers (10). The ratio of the O- and C-alkylation products is generally higher than in conventional molecular organic solvents [14 a,b]. The possibility of controlling the reaction regio-direction by modifying the ionic liquid and alkylating agent structures was demonstrated (Scheme 3). The portion of the O-alkylation products (10) increases during the transition from 1,3-dialkylimidazolium to 1,2,3-trialkylimidazolium salts. This is likely to occur due to a lack of the mobile hydrogen atom in position 2 of the imidazole cycle, capable of building hydrogen bonds with the oxygen atom of the ambident anion. The use of [bmim][$BF_4$] as a phase transfer catalyst in the $K_2CO_3$/benzene system is also accompanied by an increased yield of the O-alkylation products, if compared to similar experiments that involve tetraalkylammonium salts.



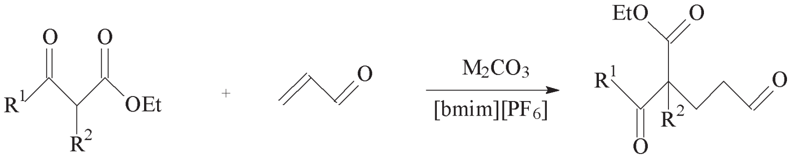
8 9 10

| Compound | R | Hal | Ionic liquid | Time, h | Temp., °C | Yield 9+10,% | Ratio 9/10 |
|---|---|---|---|---|---|---|---|
| 9a+10a | $Bu^n$ | Br | [bmim][$PF_6$] | 12 | 120 | 51 | 88/12<br>(>99/1 a) |
| 9d+10d | $C5H_{11}^{i}$ | Br | -"- | 12 | 120 | 75 | 60/40<br>(>99/1a) |
| -"- | -"- | -"- | [bmim][$BF_4$](cat)/ toluene | 12 | 110 | 45 | 67/33 |
| -"- | -"- | -"- | [bpy][$BF_4$] | 12 | 110 | 48 | 71/29 |
| -"- | -"- | -"- | [bdmim][$PF_6$] | 12 | 110 | 47 | 50/50 |
| 9e+10e | $PhCH_2$ | Cl | [bmim][$PF_6$] | 12 | 120 | 52 | 80/20 |
| -"- | -"- | -"- | [bmim][$BF_4$]/ toluene | 12 | 120 | 53 | 71/29<br>(>99/1 a,b) |
| -"- | -"- | -"- | [bpy][$BF_4$] | 12 | 120 | 53 | 80/20 |
| -"- | -"- | -"- | [bdmim][$PF_6$] | 8 | 120 | 51 | 54/46 |
| 9h+10h | Ger [c] | -"- | [bmim][$BF_4$] | 6 | 90 | 56 | 77/23 |

**[a] Ratio of alkylation products in the system EtONa/EtOH.**
**[b] Ratio of alkylation products in the system $K_2CO_3$/benzene/TEBAC.**
**[c] Ger = $(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2$**

**Scheme 3. Alkylation of acetoacetic ester (8) promoted by $K_2CO_3$ in ionic liquids.**

It has been shown that CH-acids react with a,b-unsaturated aldehydes (acrolein, croton aldehyde, and citral) in the ionic liquid [bmim][$PF_6$]. The reactions of diethylmalonate (1), ethylacetoacetate (8) and their 2-(3',7'-dimethyl-2',6'-octadien)yl (geranyl) derivatives (11) and (12) with acrolein in [bmim][$PF_6$] lead to aldehydoesters (13)-(16) (Scheme 4). A “mild” deprotonating agent $Na_2CO_3$ and ultrasonic (US) treatment of the reaction mass increases the yield of products [15].



1, 8, 11, 12

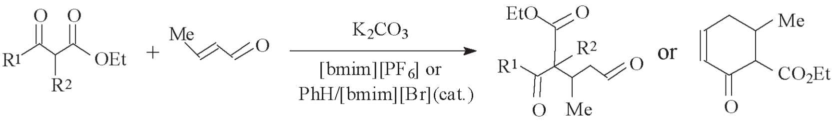
13-16

| Compound | $R^1$ | $R^2$ | M | Temp., °C | Time, h | US | Yield 13-16,$^a$ % | Return [bmim][$PF_6$], % |
|---|---|---|---|---|---|---|---|---|
| 13 | OEt | H | K | 40 | 2 | + | 46(50) | 98 |
| 13 | OEt | H | Na | 40 | 4 | - | $^b$ | 98 |
| 13 | OEt | H | Na | 40 | 4 | + | 58(50) | 98.5 |
| 14 | OEt | Ger | K | 20 | 5 | - | 55 | - |
| 15 | Me | H | Na | 20 | 4 | - | 37(47) | 97.5 |
| 15 | Me | H | Na | 40 | 2 | + | 55(47) | 98.5 |
| 16 | Me | Ger | K | 40 | 2 | + | 53 | 99 |
| 16 | Me | Ger | Na | 40 | 6 | + | 72 (61$^d$) | 98 |

**[a] The yields of 1-4 in the system $Na_2CO_3$/PhH/TEBAC (cat.) [16] are reported in brackets.**
**[b] Only acrolein polymerization products were separated from the reaction mass.**
**[c] The reaction was carried out in PhH in the presence of [bmim][Br] (cat.).**
**d The yield was cited in [17].**

**Scheme 4. Reactions of CH-acids with acrolein in [bmim][$PF_6$].**

Unlike acrolein, the croton aldehyde does not interact with malonic (1) and acetoacetic (8) esters and their 2-geranyl derivatives (11) and (12) in the [bmim][$PF_6$] medium under the action of $Na_2CO_3$. 1,4-Addition products (17) - (20) were attained either in the [bmim][$PF_6$]/$K_2CO_3$ system under exposure to ultrasounds or in the PhH/$K_2CO_3$/[bmim][Br] system (Scheme 5). Adduct 19 transforms spontaneously to cyclohexenone (19a) when the reaction is conducted in [bmim][$PF_6$], though it can be produced in the system PhH/$K_2CO_3$/[bmim][Br] (cat.) as well [15].



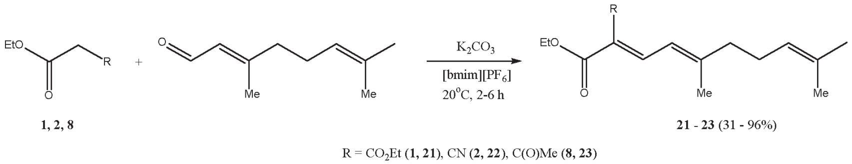
17-20 19a

| Compound | $R^1$ | $R^2$ | Temp., °C | Time, h | US | Yield 17-20,$^b$ % | Return [bmim][$PF_6$], % |
|---|---|---|---|---|---|---|---|
| 17$^c$ | OEt | H | 40 | 6 | - | 59(60) | - |
| 17$^c$ | OEt | H | 40 | 2 | + | 59(60) | - |
| 18 | OEt | Ger | 20 | 20 | - | 41 | 98.5 |
| 18 | OEt | Ger | 40 | 7 | + | 54 | 99 |
| 19$^c$ | Me | H | 40 | 3 | - | 65(48) | - |
| 19$^a$ | Me | H | 40 | 2 | + | 55(10$^d$) | 98 |
| 20 | Me | Ger | 40 | 6 | + | 56 | 98 |

**[a] Reactions were carried out in [bmim][$PF_6$] unless otherwise is indicated.**
**[b] In brackets are given yields in the system $Na_2CO_3$/PhH/TEBAC(cat.) [16].**
**[c] The reaction was carried out in PhH in the presence of [bmim][Br] (cat.).**
**[d] The yield of 19$^a$ was cited in [18, 19].**

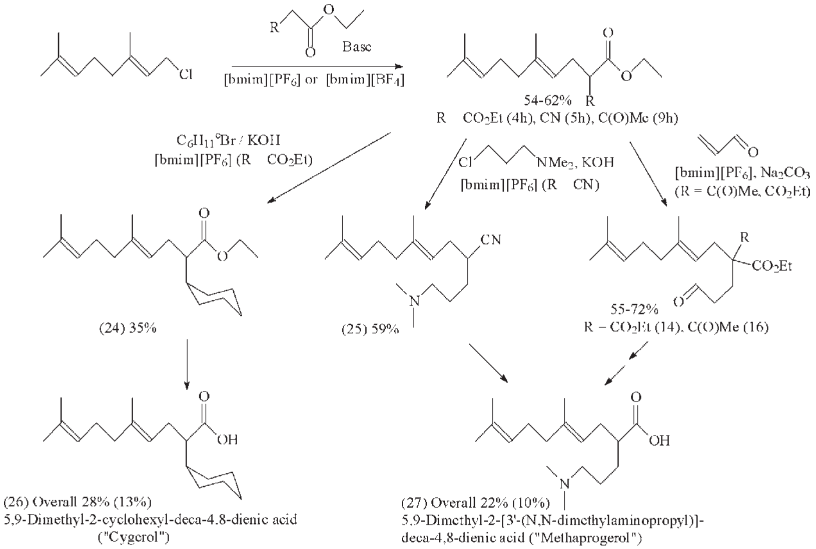
**Scheme 5. Reactions of CH-acids with croton aldehyde in [bmim][$PF_6$] and in the system PhH/[bmim][Br](cat.)._**

The interaction of esters of malonic, acetoacetic and cyanoacetic acids (1), (2) and (8) with 3,7-dimethyl -2,6-octadienal (citral), the β-carbon atom of which is bound with two bulky substituents, in [bmim][PF6] leads to 1,2-addition products (21) - (23), regardless of the CH-acid nature (Scheme 6) [15].



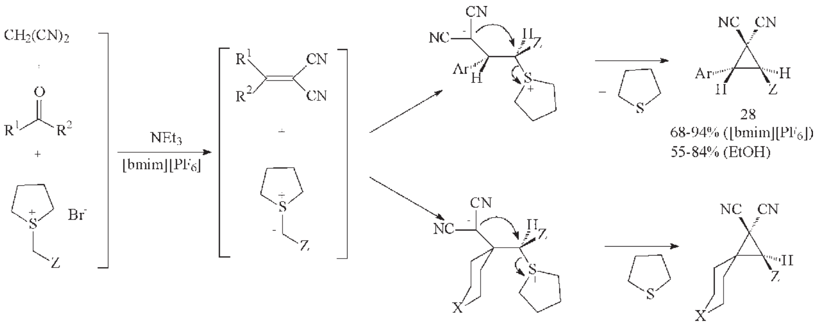
**Scheme 6. Reactions of CH-acids with 3,7-dimethyl-2,6-octadienal (citral).**

The developed synthetic alternatives were tested at the key steps of the synthesis of 2-substituted 5,9-dimethyl-4,8-dienic acid derivatives 26 and 27. Compound 26 (“Cygerol”) is used for festering and cure of burns. Compound 27 (“Methaprogerol”) promotes repair of the myocardial scars after infarction. The total yield of the target substances exceeded the yield achievable by traditional methods (Scheme 7) [14b, 15].



**Scheme 7. Synthesis of pharmaceuticals of the isoprenoid series based on the CH-acid alkylation reactions in ionic liquids.**

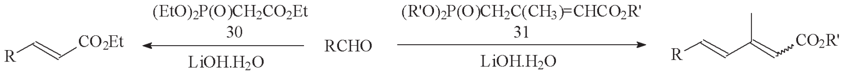
Ionic liquids were successfully utilized as solvents in a multi-component reaction of tetramethylene sulfonium salts, containing an active methylene group, with carbonyl compounds and malonic acid dinitrile. The reaction is a suitable one-step method for synthesizing functionalized cyclopropanes, which also show fungicide properties. When conducted in [bmim][PF$_6$], the reaction is characterized by higher yields of the target products (68-94% vs. 55-84% in ethanol). Probably, the ionic medium facilitates the process of tetrahydrothiophene 1,3-elimination (E$_{1,3}$) at the limiting reaction step and contributes to raising cyclopropane yields (Scheme 8) [20].



$R^1$ = H, $R^2$ = 4-$H_3COC_6H_4$, 2-$FC_6H_4$, 3,4-$F_2C_6H_3$, 2,3,4-$(H_3CO)_3C_6H_2$, $CH(CH_3)_2$;
$R_1,R_2$ = -$(CH_2)_2CH(C_4H_9^t)(CH_2)_2$-, -$(CH_2)_2N(COOC_4H_9^t)(CH_2)_2$-, -$(CH_2)_2O(CH_2)_2$-;
X = $CH(C_4H_9^t)$, $N(COOC_4H_9^t)$, O;
Z = PhCO, $Ad^1CO$

**Scheme 8. Synthesis of 1,1-dicyanocyclopropanes from malonodinitrile, carbonyl compounds and tetramethylene sulfonium salts in the ionic liquid [bmim][PF$_6$].**

In addition to the malonic acid derivatives and their analogs, methylene-active phosphonic esters are capable of fulfilling the function of CH-acids in reactions with electrophiles. We have designed a convenient technique of aldehyde olefination by activated dialkyl phosphonates (30) and (31) in the ionic liquid [bmim][PF$_6$] (Scheme 9). The reaction produces α,β-unsaturated (32a-f) and diene ethers (33), including (33a) an effective mite control sterilizing agent (Tetranychidae), hydroprene (33b) and methoprene (33c), analogs of insect juvenile hormone [21a,b]. The reactions in ionic liquids are comparable in yields and regio selectivity with corresponding phase transfer catalysis transformations, whilst the multifold use of the solvent make them more beneficial.



32a-f

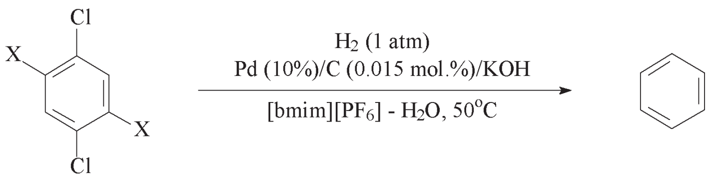
33a-c

2E/2Z = 60/40 (a), 75/25 (b), 80/20 (c)

| Compound | R | R' | Time, h | Yield, % | No. of cycle | Return [bmim][PF$_6$], % |
|---|---|---|---|---|---|---|
| 32a | $(CH_3)_2CHCH_2$ | $C_2H_5$ | 2 | 70 | 1 | 89 |
| 32b | Ph | $C_2H_5$ | 4 | 78 | 1 | 92 |
| 32b | Ph | $C_2H_5$ | 4 | 81 | 2 | 91 |
| 32c | (E) PhCH=CH | $C_2H_5$ | 6 | 71 | 3 | 93 |
| 32d | $C_3H_5^c$ | $C_2H_5$ | 2 | 68 | 4 | 94 |
| 32e | 2-Pyridyl | $C_2H_5$ | 3 | 74 | 5 | 93 |
| 32f | $(H_3C)_2C=CH(CH_2)_2CH(CH_3)CH_2$ | $C_2H_5$ | 7 | 65 | 6 | 92 |
| 33a | $(H_3C)_2CHCH_2$ | $C_2H_5$ | 6 | 48 | 1 | 91 |
| 33b | $(H_3C)_2CH(CH_2)_3CH(CH_3)CH_2$ | $C_2H_5$ | 10 | 75 | 2 | 93 |
| 33c | $(H_3C)_2C(OCH_3)(CH2)_3CH(CH_3)CH_2$ | $C_3H_7^i$ | 10 | 81 | 1 | 90 |

**Scheme 9. Olefination of aldehydes by activated dialkyl phosphonates in the ionic liquid [bmim][PF$_6$].**

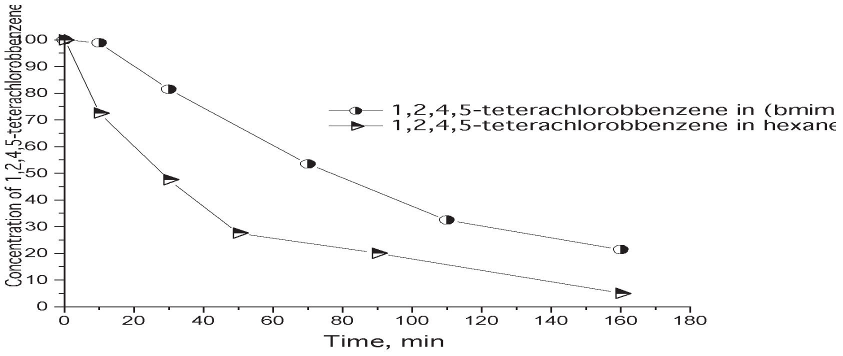
It is known that imidazolium salts are able to increase the activity of catalysts based on transition metals [3,4]. Lately we have started researching the processes of hydrodechlorination of polychloroaromatic compounds on transition metal catalysts in ionic-liquid media from the imidazole series. 10% Pd/C-catalyzed hydrodehalogenation of di- and tetrachlorobenzenes to benzenes under the action of hydrogen was shown to proceed 2 - 3 times faster in the ‘[bmim][PF$_6$]-water’ system than in alcohols or in the ‘water-nonpolar organic solvent’ system (Schemes 11 and 12). The discovered effect is likely to be useful in designing high performance technologies for the detoxication of hazardous polychlorinated organic congeners (polychlorobiphenyls, pesticides, dioxins, etc.) [22].



| X | Complete hydrodehalogenation time, h<br>[bmim][$PF_6$] - $H_2O$ | <br>Pr$^i$OH | <br>Hexane - $H_2O$ |
|---|---|---|---|
| H | 0.5 | 1.0 | 1.5 |
| Cl | 1.5 | 2.0 | 4.0 |

**Scheme 11. Pd-catalyzed hydrodehalogenation of polychlorobenzenes in [bmim][HSO4].**

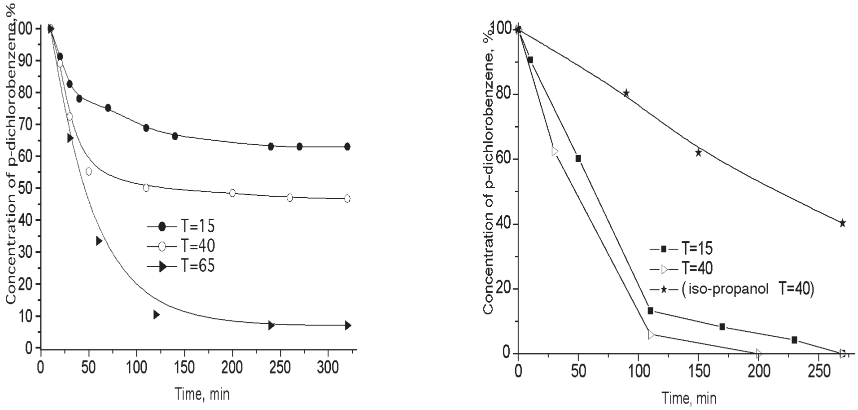
|  | Catalyst | Solvent | Reaction temperature, °C | Yield, %<br>Trichloro-benzenes | <br>1,2,4,5-tetrachloro-benzene | <br>p-dichloro-benzene | <br>o- dichloro-benzene |
|---|---|---|---|---|---|---|---|
| 1 | 10% Pd/C | hexane | 50 | 32.5 | 16.6 | 9 | 29.8 |
| 2 | 1,25% $Fe_{60}Pd_{40}$/C | hexane | 50 | 10 | 85 | 0.42 | 3.2 |
| 3 | 10% Pd/C | [bmim][$PF_6$] | 50 | 53.2 | 5 | 18.6 | 26.6 |



**Scheme 12. Hydrodehalogenation of 1,2,3,4-tetrachlorobenzene to benzene under the action of hydrogen in various solvents.**

**Hydrodechlorination of 1,4-dichlorobenzene in [bmim][$BF_4$] at varying reaction temperature (°C )**

**Hydrodechlorination of 1,4-dichlorobenzene in [bmim][$PF_6$] at varying reaction temperature (°C)**

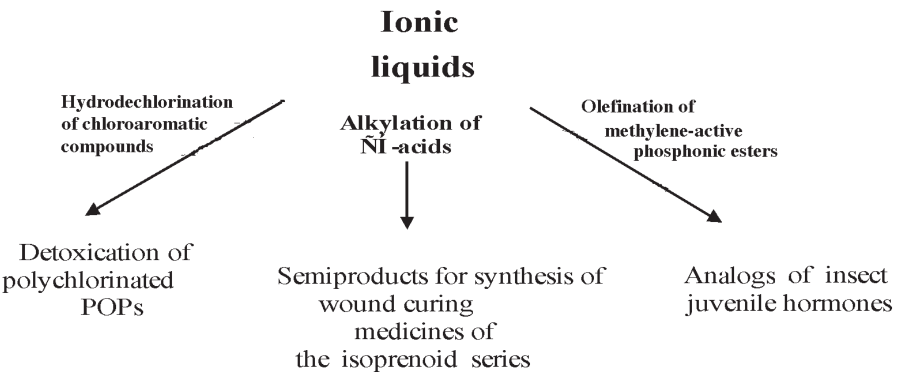


**[bmim][$BF_4$] - N-methyl-N-butyl-imidazolium tetrafluoborate**

**bmim][$PF_6$] - N-methyl -N-butyl - imidazolium hexafluophosphate**

**Scheme 13. Hydrodehalogenation of 1,4-dichlorobenzene to benzene under the action of hydrogen in the presence of 10% Pd/C catalyst in ionic liquids.**

Thus, we have studied the reactions of CH-acids promoted by bases and the processes of hydrodechlorination of chloroaromatic compounds in ionic liquid media. The developed methods were used to prepare biologically active substances for pharmaceutical and agricultural applications, as well as for the toxic polychlorinated matter degradation processes. The obtained results evidence the valuable opportunities given by the use of ionic liquids in liquid-phase chemical reactions. It is possible to safely forecast that new fundamental results and novel technologies – based on the use of these unusual solvents and catalysts – are going to emerge in the near future.



**Ionic liquids**

**Hydrodechlorination of chloroaromatic compounds**

**Alkylation of ÑI -acids**

**Olefination of methylene-active phosphonic esters**

Detoxication of polychlorinated POPs

Semiproducts for synthesis of wound curing medicines of the isoprenoid series

Analogs of insect juvenile hormones

## REFERENCES

1. *"Ionic liquids in Synthesis"* Ed. by P. Wasserscheid and T. Welton, Wiley-VCH, 2003, pp.1-363.
2. T. Welton, *Chem.Rev.* 1999, 99, p. 2071-2083.
3. H. Olivier-Bourbigou, L. Magna, *J.Mol.Catal. A: Chemical* 2002, 182-183, pp. 419-437.
4. D. Zhao, M. Wu, Y. Kou, E. Min. *Catalysis Today* 2002, 74, pp. 157-189.
5. U. Kragl, M. Eckstein, N. Kaftzik, *Current Opinion in Biotechnology*, 2002, 13, pp. 565-571.
6. A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, *J.Phys.Chem.* B 2003, 107, pp. 4024-4033.
7. D.A. Costa, W.H. Smith, W.J. Warren, *"Plutonium chemistry in room temperature ionic liquids"*, Abstract Pap., Am.Chem.Soc. 221st meeting, 2001, IEC-059.
8. P. Wang, S.M. Zakeeruddin, P. Comte, I. Exnar, M. Grätzel, *J. Am. Chem. Soc.* 2003, 125, pp. 1166-1167.
9. L.C. Branco, J.G. Crespo, C.A.M. Afonso, *Chem. Eur. J.* 2002, 8 (17), pp. 3865-3871.
10. M. Freemantle, *Science Technology* 2000, 78 (20), pp. 37-50.
11. S.N.V.K. Aki, J.F. Brennecke, A. Samanta, *Chem. Commun.* 2001, pp. 413-414.
12. R.R. Deshmukh, R. Rajagopal, K.V. Srinivasan, *Chem. Commun.* 2001, pp. 1544-1545.
13. G.V. Kryshtal, E.P. Serebryakov, *Russ. Chem. Bull.* 1995, 44, pp. 1785-1804.
14. (a) G.V. Kryshtal, G.M. Zhdankina, S.G. Zlotin, *Mendeleev Commun*. 2002, pp. 57-59;
    (b) G.V. Kryshtal, G.M. Zhdankina, S.G. Zlotin, *Russ. Chem. Bull.* 2004, 53 (3), pp. 652-658.
15. G.V. Kryshtal, G.M. Zhdankina, I.V. Astakhova, S.G. Zlotin, *Russ. Chem. Bull.* 2004, 53 (3), pp. 647-651.
16. G.V. Kryshtal, V.V. Kulganek, V.F. Kucherov, L.A. Yanovskaya, *Synthesis*, 1979, pp. 107-109.
17. V.V. Kulganek, G.V. Kryshtal, L.A. Yanovskaya, *Izv. Akad. Nauk, Ser. Khim.*, 1980, 9, 2161-2164, Chem. Abstracts 1981, 94, p. 83576g.
18. E.D. Bergmann, R. Papport, V. Ginsburg, in *Organic Reactions*, 10, Wiley & Sons, New York, 1959, pp. 179-555.
19. S.M. Mukherjee, B.K. Bhattacharyya, *J Indian Chem. Soc*. 1946, 23, p. 451.
20. A.A. Shestopalov, L.A. Rodinovskaya, A.M. Shestopalov, S.G. Zlotin, V. Nesterov, *SYNLETT* 2003, 15, pp. 2309-2312.
21. (a) G.V. Kryshtal, G.M. Zhdankina, S.G. Zlotin, *Mendeleev Commun.* 2002, pp.176-178;
    (b) S.G. Zlotin, G.V. Kryshtal, G.M. Zhdankina, P.A. Belyakov, E.P. Serebryakov, *Russ. Chem. Bull.* 2004, 53 (3), pp. 659-664.
22. S.S. Yufit, S.G. Zlotin *"Destruction of persistent organic pollutants. Chemical alternatives"*, Hazardous Halo-Aromatic Pollutants: Detoxification and Analysis, Proceedings of the International Workshop, Venice, 12-14 May 2002, pp. 30-36.

# ENVIRONMENTAL CATALYSIS ACHIEVEMENTS AND OPPORTUNITIES

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Jacques Yves Cousteau once said that the globe reminds him "a car without the exhaust pipe speeding alone in the outer space". We dump wastes right into the environment where we live. Man is already conscious of negative effects of his vigorous and, in many respects, uncontrolled activities. In the 21st century, researches focused on the extensive use of environmentally-friendly catalytic technologies, that help to minimize or completely avoid generation of industrial waste, assumed strategic significance. Green chemistry, as a new conception, regards the issue of waste prevention of its generation source with particular concern.

Contemporary power supply creates conditions for the existence of civilized mankind and, at the same time, is the core source of environmental pollution, primarily the atmospheric one. High global consumption of relatively "clean" energy resources, such as natural gas and crude oil, is inconsistent with their proportion in world reserves of organic fuels, where coal predominates. Because of that, great attention has been recently paid to restructuring of energy consumption and production of chemicals, first of all, automotive fuels, and to refocusing from gas and oil to coal or other alternative sources. It should be pinpointed that a switchover to coal as a feedstock of chemical or power industries will entail a drastic build-up of the environmental load, since its processing generates larger amounts of hazardous waste. Hazardous waste management calls for various sophisticated technical solutions, of which most promising are catalytic technologies.

Actually catalytic technologies permeated into all chemical production types. To a large extent, they govern both the everyday life of modern society and the future of our civilization. The advancement of environmental catalysis is generally guided by global environmental policy and national programs. Environmental legal acts adopted in the USA, European Union and other developed countries as well as the Kyoto Protocol that limits $CO_2$ air emissions, kick-started catalytic research re-orientation to development of technologies for producing top quality sulphur- and aromatic hydrocarbons-free gasoline and diesel fuels, as well as high performance alternatives for nitrogen and sulphur oxides removal from gas emissions of heat power plants and transport exhausts [1]. In Russia, remarkable for its high science and technology potential, leading research centres are engaged in basic researches targeted on design of effective catalytic systems and their application, through new technologies, for neutralization of toxic chemicals, as well as at development of environmentally clean waste-minimization processes.

For denitrification of emissions from heat power plants, a method of selective catalytic reduction (SCR) of NOx by ammonia has been recently developed and introduced [2]. However, the SCR technology that comprises a highly toxic reagent, i.e. ammonia, is not environmentally perfect. In addition to ammonia storage and transportation, it needs application of unfailing and precise metering, control and post-combustion methods. A technology of homogeneous non-catalytic removal of nitrogen oxides by ammonia reduction has even more constraints if compared to SCR, as it demands regular distribution of ammonia across the combustion region at a temperature of 1000°C. It is quite a challenge in practice and prevents from achieving high performance of the process. The same disadvantages are inherent to a carbamide technique for NOx reduction, which incorporates an additional step associated with a high recycled water consumption and wastewater neutralization.

To this end, both in Russia and worldwide, ammonia-free alternatives for NOx neutralization with the employment of noble metal-free catalysts are being intensively developed. Among them, the most attractive appears to be the selective catalytic reduction of nitrogen oxides using hydrocarbons as reducing agents.

Desulphurization processes are more complicated than denitrification ones, because of absorption, and “wet” methods being predominately used to clean gases from sulphur oxides. They consume considerable recycled water amounts, thus increasing complexity of the treatment technology.

In compliance with the regulations of the Russian Federation (RF), both denitrification and desulphurization units for flue gas have to be installed at each heat power plant. However, successive consecutive removal of sulphur and nitrogen oxides is highly energy-consuming and, sometimes, even technically unfeasible. For this reason, a method that combines nitrogen and sulphur oxides removal in one set with production of mineral fertilizers, which is currently under development in Russia and other countries, seems to have higher opportunities in flue gas treatment.

In countries with developed economies, air pollution control is supported both by legal acts and significant investments to catalytic and related technologies for treatment of gas emissions from power generating, manufacturing industries, and transports. Nowadays, gas treatment catalysts account for 33% of total cost of commercial catalysts, i.e. about 10 billion USD [3].

Noble metal-supported catalysts for treatment of gasoline engine exhausts rank first by cost. A benefit of the supported catalysts is provided by their high activity under heavy oxidation conditions and at high space velocities of gas flow. Further researches in this area are targeted at expanding the temperature range where they exhibit maximum activity. It may be attained either by introducing various promoters, combinations of noble metals with transition ones, or by selecting an appropriate support.

Cation-substituted zeolites show great potential as catalysts for selective reduction of nitrogen oxides by hydrocarbons, methane inclusive. Ways of zeolite catalyst improvement – in terms of selective catalytic reduction of $NO_x$ – imply the creation of new specimens, capable of exhibiting their activity at low temperatures and retaining structural stability to prevent hydrodynamic deactivation.

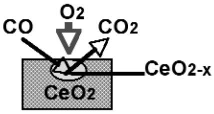
A great number of publications deal with the catalytic properties of both blocked and supported metal oxides. One of the promising areas of environmental catalysis is the screening of the properties of the existing catalysts, including commercial ones, and design of complex catalytic systems for processes in which catalysis is still unavailable. Of particular interest are the multi-component and especially the multi-phase catalysts, including perovskite-based ones, that possess desirable physico-chemical properties. Such systems make it possible to split a complex reaction into separate steps, each step being accelerated by a single catalyst. This dramatically improves the process selectivity. Catalytic systems in form of mechanical mixtures, in some cases, display synergic properties, which considerably increase their activity [4].

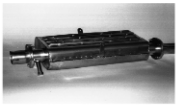
A few catalysts based on noble metals are utilized for complex treatment of exhausts from motor vehicles. Using three-ways catalysts (TWC) such treatment includes three simultaneous reactions: reduction of $NO_x$ and CO and oxidation of hydrocarbons. Yet, the ability of these catalysts to display high activity in stoichiometric mixtures – that correspond to the composition of exhausts from carburettor engines – constrains their applications in treatments conducted in oxygen excess, particularly for diesel engines. For this reason, priority is given to the researches focused on the development of catalysts that are less sensitive to changes in the composition of gases to be treated. Rather promising in this respect are catalytic systems incorporating transition metals characterized by different oxidation states, as active components and an “oxygen-accumulating” component, e.g. $CeO_2$, capable of reversible $O_2$ release/acquisition depending on the gas mix composition; this feature considerably expands the range of their applications (see Scheme 1).

A recent solution implemented for raising diesel exhaust treatment efficiency is providing the catalyst's formulation with an additional component that serves as a “reservoir” for $NO_x$. In the oxidizing medium, NO on the catalyst oxidizes to $NO_2$, which is then absorbed by BaO and the generated barium nitrate decomposes to molecular nitrogen and BaO in the reducing medium (Scheme 1).

Key catalysts based on noble metals (Pt, Pd, Rh, and Ir) for CO, $C_xH_x$ and $NO_x$ neutralization

**$CeO_2$ – $O_2$ accumulating oxide**





**BaO – $NO_x$ "reservoir"**

In the oxidizing medium, NO on $Pt/BaO/Al_2O_3$ oxidizes to $NO_2$, which is then absorbed by BaO:

$$BaO + 3NO_2 \rightarrow Ba(NO_3)_2 + NO$$

In the reducing medium,

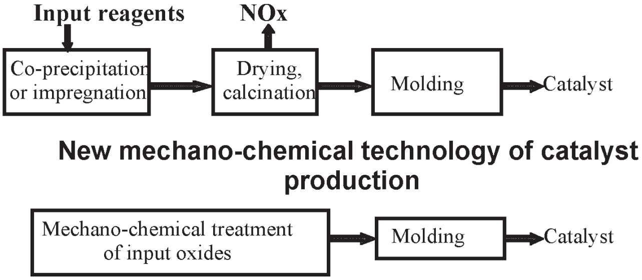
$$Ba(NO_3)_2 + CxHy(CO) \rightarrow BaO + N_2 + CO_2 + H_2O$$

**Scheme 1. New approaches to TWC for automotive transport**

Diesel engines burn "poor" blends containing considerable excessive oxygen that surpasses the amount dictated by the stoichiometry of the reaction $C_nH_m + O_2$. In such blends, nitrogen oxides typically are oxidized rather than reduced. This explains why no adequate solution has been so far found for the problem of $NO_2$ removal from diesel exhausts. Moreover, in reality, exhaust gases incorporate water vapours, sulphur oxides and some other admixtures, such as polyaromatic hydrocarbons and particulates, which negatively affect both the activity and selectivity. These factors have to be addressed by developers of catalysts for $NO_x$ removal.

One of possible options is the use of columnar or pillarated clays. Such kind of materials are based on zirconium oxide. They provide good gas dynamics, are thermally stable, and resistant to water and $SO_2$. Due to low acidity, they tend less to sinter than common clays and zeolites. During last years, Russian chemists have been intensively studying the columnar clay catalysts. They are catalysts of new generation and have a high potential in deNO$_x$ processes, especially for diesel emission treatment.

Researches focusing on high performance catalysts include the development of new environmentally perfect methods and technologies for catalysts preparation. For instance, a mechano-chemical method allows phasing-out of drying and calcination steps, where nitrogen oxides are released under decomposition of nitrates used for support impregnation (see Scheme 2). This technology enables to prepare catalysts of various compositions with new unique properties, that exceed their commercial analogues produced by traditional impregnation and co-precipitation techniques. High performance catalysts for neutralization of CO, organic admixtures and NO$_x$ have been recently obtained by the mechano-chemical method.



**Scheme 2. Main technological steps of existing catalyst production.**

The mechano-chemical method of catalyst preparation appears to be promising for the following reasons: it is environmentally clean, allows to set up manufacture of catalysts with any preset composition and, hence, devise industrial technologies for gas emission detoxification over a short period of time.

Next-generation catalysts are prepared on the basis of nanotechnologies using methods of cryochemistry, plasmochemistry, alkoxotechnology, synthesis in conditions where solvents are in their supercritical state, etc. Tests of these catalysts in redox reactions of environmental catalysis with the participation of nitrogen, carbon, sulphur oxides, and other toxic substances evidence that listed methods have great potential in tackling urgent problems of pollution abatement. For instance, Cu-Co catalysts prepared in Russia using nanotechnologies (by cryochemical method or in flow-type set using supercritical water) are 2-2.5-times more active than their analogues, obtained by traditional impregnation and co-precipitation (Table 1).

**Table 1. Temperature of 100% conversion of CO in the reaction CO + $O_2$ , space velocity 10,000 h-$_1$**

| No. | Catalyst and its preparation method | Temperature of 100% conversion of CO, °C |
|---|---|---|
| 1. | Cu-Co /$Al_2O_3$ (cryochemical method) | 90 |
| 2. | Cu-Co/Y-Ce-Zr oxides (in supercritical water) | 100 |
| 3. | Cu-Co/Y-Ce-Zr oxides (traditional impregnation method) | 250 |

Another way of mitigating industrial pollution is the development of environmentally perfect alternatives for heat generation and production of various chemicals.

Among them, for example, are new processes developed in Russia: heat generation by catalytic surface fuel combustion and incineration of toxicants in the catalytic surface combustion operative mode. The developed method of flameless combustion of fuels (methane, propane, butane, kerosene, etc.) on block catalysts, with a perofskite structure, actually ensures full absence of $NO_x$ and CO in the combustion products. The process is alternative to flame burning of fuels, characterized by considerable emissions of toxic ingredients.

For surface fuel combustion, methods of synthesizing fine-dispersed active components from available raw materials were elaborated. On their basis, block cellular catalysts with different geometry were prepared, characterized by high catalytic activity, thermal stability, and heat shock resistance. These perovskite-based catalysts are also likely to find applications in detoxification of industrial gas emissions. They possess chemical stability in the presence of hydrofluoric and hydrochloric acid vapours and impart higher stability to the processes. Due to that, they are applicable for post-combustion of fluorine and chlorine organic compounds in Freon incineration and may significantly contribute to solve the dioxin problem.

Thus surface combustion of fuels has a high potential and may be considered as an environmentally clean alternative for heat recuperation in hydrocarbon fuel burning, for neutralization of industrial emissions and motor transport exhausts, as well as for incineration of super-toxicants at landfills.

In addition to the described catalytic technologies, there are other attempts to address the issue of exhausts-caused pollution, including further modifications of the engine design, additional air supply to raise fuel combustion efficiency, etc. All these techniques merely bring down concentrations of toxicants in exhausts, but do not totally eliminate them.

At present, new fuel cells have been proposed as a promising energy source to replace internal combustion engines. Their mode of operation is based on generating electricity by means of the hydrogen oxidation reaction occurring on a membrane catalyst. However, the need of onboard storage of hydrogen obstacles the use of such vehicles. This motivated the development of a system to combine a fuel cell with a catalytic reformer, where hydrocarbon fuel (gasoline, methanol, etc.) is converted to hydrogen-enriched gas. In Russia, there are ongoing researches about the creation of a new hydrogen fuel cell type for motor vehicles. First prototypes show good environmental performance. It is quite probable that in the near future cars will release only air and water steam rather than toxic gases.

In 2000, at the exhibition in Brussels, *Chrysler* demonstrated a fuel cell (methanol) sedan NECAR 5. This model offers a combination of advantages, such as the internal combustion engine capacity range, low fuel consumption, low noise and environmentally clean exhaust. For the time being, these cars are not cost-competitive with traditional automobiles. Yet, owing to environmental considerations, they will overcome their competitors in future.

Therefore, the following directions in the evolution of environmental catalysis may be singled out:

- combinatory catalysis, including screening of the properties of available catalysts, with a view of their use in environmental solutions;
- new synthetic methods for preparation of high performance catalysts, including nanomaterials, based on environmentally-friendly technologies;
- co-processes to integrate desulphurization and denitrification of gas emissions with production of mineral fertilizers facilitating atmospheric nitrogen fixation;
- alternative technologies of fuel combustion under the flameless deep catalytic oxidation conditions with simultaneous destruction of toxicants;
- next-generation engines with environmentally clean exhausts.

In conclusion, it should be particularly emphasized that environmental protection must be regarded as a problem combined with economic, energetic and demographic aspects [5, 6]. Poverty of the three forth of the Earth's population is one of the main causes of the environmental load and global pollution growth. Today, 20% of the world's population enjoys 85% of the planet's total material comforts and resources; 75% of the global population live in poverty; 1.3 billion people live in absolute poverty; unemployed persons sum up to 120 millions; 1 billion people are illiterate; almost 2 billions do not use electricity; 1.5 billion people have no access to safe potable water sources. In Russia, raw material resources are utilized inefficiently: average energy consumption per production unit is 2.5-3 times higher than in many developed economies. Sixteen Russian regions, which together occupy about 15% of the country's surface, are characterized by marginal environmental conditions.

This global situation slows down the progress of the development of advanced technologies, including environmental catalysis, and leads to ever-growing hazardous emissions in the environment. Russia still retains a high-level educational and intellectual potential of nature-use specialists both in industry and R&D. However, without sustenance, this potential may fade away. Then the uncontrolled barbaric consumption of natural resources will result in the emergence of irremediable "ecological ulcers" on the surface of our beautiful planet, making it unsuitable for further living.

## REFERENCES

1. V.Krylov. Catalysis on the verge of 21st century. Some forecasts. *Russian Chemical Journal.* 2000, т.44, 4, p. 53.
2. Yu.S. Khodakov. Nitrogen Oxides and Heat Power Engineering. Problems and Solutions. M.: OOO EST-M, 2001, 432 p.
3. L.M. Kustov and O.V. Krylov. Catalysis on the boundary of millenniums: achievements of the past and outlook for the future. *Russian Chemical Journal*. 2000, V. 44, 2, p. 3.
4. L.S. Glebov, A.G. Zakirova, V.F. Tretyakov, T.N. Burdeinaya, G.S. Akopova. State-of-the-art in the research on catalytic transformations of $NO_x$ to N2. *Neftekhimia (Petrochemistry)*, 2002, V. 42, 3, p. 163.
5. Russian Statistics Annual Bulletin. 2000, 8, p. 266.Voprosy Statistiki (Statistics Issues). 2000, 10, p. 23.

# RUSSIAN DEVELOPMENTS IN THE FIELD OF NEW CATALYSTS AND PROCESSES OF SELECTIVE REDUCTION OF NITROGEN OXIDES BY HYDROCARBONS IN OXYGEN EXCESS

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Studies focused on design of new catalysts and catalytic processes for elimination of nitrogen oxides from exhaust gases emitted by automobiles and industrial facilities. Such contamination sources are of critical importance in terms of environment. They constitute a considerable part of green chemistry investigations worldwide, including Russia. It is essential to develop new processes that could possibly replace selective catalytic reduction (SCR) of nitrogen oxides by ammonia; a costly and environmentally unsafe reaction. Considering emissions characterized by a large oxygen excess (such as exhausts from diesel engines, HPPs, etc.), an attractive alternative may be the selective catalytic reduction of nitrogen oxides by hydrocarbons (SCR-HC), independently proposed by Iwamoto [1,2] and Held [3,4]. Hundreds of publications and patents, including a few reviews [5-11], have been devoted to this subject. This paper provides results attained in this area by a team of scientists from leading Russian catalytic research centres. These joint researches have been carried out since early 1990s.

Detailed, in situ inclusive, studies on the mechanism of reactions with both paraffins and olefins, used as reductants, showed that systems containing transition metal cations provide highly efficient nitrogen oxide elimination, at high gas hourly space velocities (GHSV), under realistic conditions [12-21]. Key intermediates here are strongly bound nitrite-nitrate complexes localized on coordinately unsaturated surface centres. By combining some transition metal cations with platinum or silver, it is possible to achieve conjugation between stages of nitrogen oxides and hydrocarbons activation. That also allows effective generation of nitro-organic compounds, i.e. nitrogen-, carbon- and oxygen-containing intermediates. The transformation of these intermediates with the participation of surface acid sites affects selectivity of the formation of an undesirable by-product: the nitrous oxide. These results [22] served as grounds for formulating principal requirements for the properties of active sites, including their spatial distribution on the support. This review will basically discuss approaches to the targeted synthesis of practicable catalysts in the context of the formulated requirements.

Active components based on cation-substituted ZSM-5 zeolites and $Al_2O_3$-supported cations of transition metals (copper and cobalt) [12-26] are mainly considered here. The impact on the active components performance of such factors in SCR-HC is here elucidated, with regard to the clustering of transition metal cations on supports and the acidity of the supports themselves. Approaches to the stabilization of the zeolite structure are also discussed, as well as the clustering of transition metal cations within zeolite channels, under hydrothermal conditions, via introduction of alkali-earth cations [27-28].

The study of new systems characterized by stability under real conditions of exhausts - in terms of water and sulphur dioxide content - shifted our attention to systems with zirconium cations, which show great potential for designing new advanced catalysts. Such systems include mesoporous catalysts based on partially stabilized $ZrO_2$ [29-38], ultra-microporous clays pillared by $ZrO_2$ nanoparticles [36-49], and complex zirconium framework phosphates with cations of transition metals, which may be both supported or incorporated in the framework [50-52].

For these new systems, procedures of supporting nano-structured active components have been developed. They consist of cations of transition metals (their clusters) with juxtaposed clusters of platinum group metals. Optimal active components were either extruded as bulk monoliths – with addition of a binder – or supported on various monolithic substrates. In realistic conditions, at GHSV up to 100,000 $h^{-1}$ and with the use of propane, propylene and decane as reducing agents, these catalysts ensure removal of up to 80% of nitrogen oxides without noticeable nitrous oxide generation and loss of activity in time. Such catalysts are covered by a number of Russian patents [27, 28, 37, 48, 49].

The experimental procedures and sample research methodology were detailed in the original publications [12-44, 50-54].

## 2. RESULTS AND DISCUSSION

### 2.1. NATURE OF ACTIVE SITES

#### 2.1.1. Supports

In this context, an active site can be defined as a coordinately unsaturated cation, i.e. Lewis acid site, on which reactive molecules, such as oxygen and nitrite-nitrate complexes, are stabilized and which is capable of activating the hydrocarbon molecules by itself.

Such supports – as $ZrO_2$ and $\gamma$-$Al_2O_3$ – are able to provide sufficiently high levels of nitrogen oxide conversion under their selective reduction by hydrocarbons at high temperatures (Fig. 1), even in humid reaction mixtures. Moreover, for the zirconium oxide system, water even enhances the catalyst performance (Fig. 2). Therefore, the nature of the active sites of those supports is certainly of interest as well.

For both these oxides, the activation of hydrocarbons was shown to proceed without participation of nitrite-nitrate groups, most probably, on Lewis acid sites, i.e. on coordinately unsaturated aluminium and zirconium cations [12, 24, 29]. Since C-H bond breaking on the acid site is rather an energy-demanding stage, this explains the need of high temperatures for these oxides to exhibit noticeable catalytic activity. For $\gamma$-$Al_2O_3$ , the most likely active sites are tetra-coordinated aluminium cations that display a higher acidity. Such cations are present as regular centres of (100)- and (111)- faces of $Al_2O_3$ with a spinel structure [55]. These low-coordinated sites may also emerge on other faces due to the presence of surface defects. Activated hydrocarbon fragments react with nitrite-nitrate groups yielding organic nitro-compounds as intermediates [22]. A high thermal stability of bidentate nitrate complexes, with maximum desorption temperature of approx. 500°C ($T_{max}$ of main $NO_x$ TPD peak corresponding to their decomposition), allows to retain a rather high surface covering by these key intermediates at temperatures which favour an easy activation of hydrocarbons. When nitrogen oxide is added into the hydrocarbons mixture with oxygen [24, 29], some hampering of the hydrocarbons consumption confirms that nitrate complexes can also be stabilized on coordination-unsaturated surface cations of those oxides, making them inaccessible to hydrocarbon molecules.

For highly dispersed $ZrO_2$ samples, it is possible to alter the concentration and properties of the active surface sites, i.e. coordination-unsaturated Zr4+ cations, by incorporation of low-charge doping cations into the lattice [30-34] and by changing the phase nature (monoclinic, tetragonal or cubic) or particle sizes [29, 41, 42]. Modification of the properties of coordinately unsaturated sites on the $ZrO_2$ surface is primarily reflected in variation of nitrite-nitrate complexes types and their bonding strength. For instance, in $ZrO_2$ nanoparticles fixed in the interlayer space of pillared clays, weakly bound nitrite complexes are predominantly found ($T_{max}$ of $NO_2$ peak corresponding to their decomposition is approx. 380°C). This is related to a high hydroxylation degree of $ZrO_2$ nanoparticles, which increases coordination saturation of adsorption sites-zirconium cations [41,42].

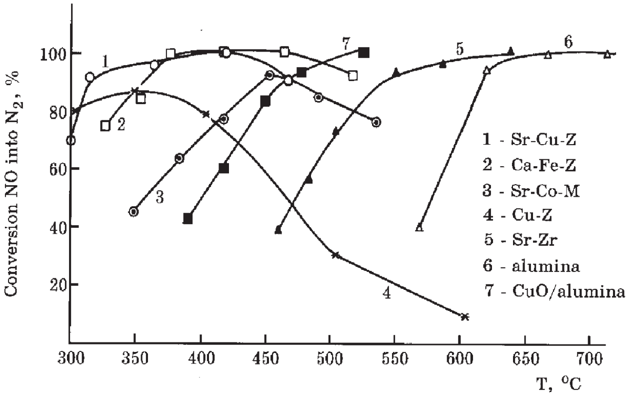

**Fig. 1. Typical temperature dependences of $NO_x$ conversion in $N_2$ under SCR by propane for catalysts with various composition: Z - ZSM-5, M - mordenite. The reaction mixture composition: 0.1% NO +0.1% $C_3H_8$ + 1% $O_2$ in He.**

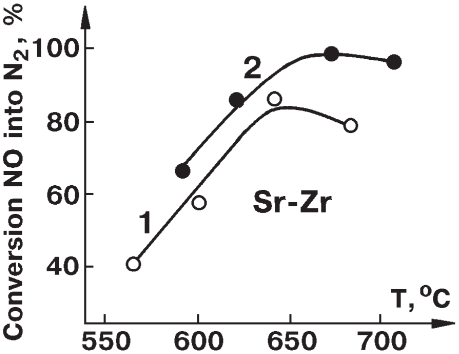

**Fig. 2. Influence of water addition to the reaction mixture on the degree of nitrogen oxide conversion to $N_2$ in the course of SCR by propane on $ZrO_2$ partially stabilized by Sr (5 at. %): 1 - standard reaction mixture (0.1% NO +0.1% $C_3H_8$ + 1% $O_2$ in He), 2 - the same plus 3% $H_2O$.**

At the same time, for bulk dispersed $ZrO_2$ samples (particle size exceeding hundreds of angstroms), dominating are nitrogen oxide adsorption forms, such as nitrate complexes [22, 29, 53]. In the case of the tetragonal $ZrO_2$ phase, monodentate complexes prevail, they decompose into NO and oxygen around 500°C. Bridged nitrate complexes which decompose with nitrogen dioxide release at lower temperatures (≈50°C less) were detected for the monocline phase characterized by a high degree of coordinational unsaturation of zirconium surface cations [22, 29].

The addition of doping cations of alkali-earth metals (Ca, Sr and Ba) and Al cations allows to stabilize the tetragonal $ZrO_2$ phase and its specific surface area, as well as to change the concentration of coordinately unsaturated sites and their properties [30-32, 35]. In the majority of cases, the optimal dopant amount which corresponds to a high density of coordinatively unsaturated surface sites does not exceed a few atomic percents. A partial blocking of the surface of $ZrO_2$ particles by segregated alumina clusters occurs at a relatively high content (over 10%) of doping Al cations [35]. In the case of added calcium and strontium cations, a rise in their concentrations causes reconstruction of the surface layer of partially stabilized $ZrO_2$ into a perovskite-type one. This is accompanied by a drop in surface concentrations of both Broensted and Lewis acid sites [30-32], thus decreasing activity in the propane $NO_x$ SCR especially at high temperatures (Table 1). At the same time, such reconstruction is not energetically favoured for bigger Ba cations [30] and due to that activity grows along with the Ba content (Table 1).

The relaxation of coordination polyhedra in the fluorite structure is also important for partially stabilized $ZrO_2$, when doping cations - differing in size from the zirconium ones - are introduced. This is reflected in the average strength of the zirconium-oxygen bond and reactivity of the key intermediates, nitrite-nitrate complexes. As shown in [16], for the $ZrO_2$ samples with low concentration of doping alkali-earth metal cations (5%), the higher is the charge on the coordinately-unsaturated zirconium cation (evaluated by the constant of the triplet splitting of the EPR spectrum of the TEMPO nitroxyl radical), the higher is the thermal stability of nitrate complexes (maximum temperature of the thermodesorption peak). The pattern of this phenomenon is Sr < Ca < Ba. From the data of Table 1, we can see that specific catalytic activity also decreases in the same way at 450°C.

**Table 1. Kinetic parameters of $NO_x$ selective catalytic reduction by propane in oxygen excess [30].**

|  | Alkali-earth cation content (at. %) |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| Kinetic | Ca |  |  |  | Sr |  |  | Ba |  |  |
| Parameters | 1.5 | 5 | 10 | 25 | 2 | 5 | 10 | 5 | 10 | 25 |
| Ea, kcal/mol | 34 | 16 | 13.0 | 9.0 | 28 | 30 | 20 | 20 | 22 | 18 |
| Kx103, 450 °C | 1.3 | 3.0 | 2.9 | 3.6 | 2.4 | 3.4 | 1.56 | 1.18 | 2.5 | 3.9 |
| Kx103, 550 °C | 20 | 12 | 9 | 6 | 21 | 40 | 10 | 5 | 15 | 17 |

The strength of the nitrate complexes bond with the surface evidently depends not only on the effective charge of the zirconium cation, but also on the strength of its bond with the surface oxygen incorporated in such complexes. For non-reducible Zr oxides, it is difficult to apply conventional methods, such as oxygen temperature-programmed desorption (TPD) and reduction (TPR) by hydrogen, to evaluate the bonding strength of the surface oxygen. At the same time, mass-spectrometry of secondary ions (SIMS) allows assessment of the relative strength of the oxygen-cations bond by using ratio of the ion currents corresponding to $Me^+$ and $Meo^+$ fragments (Table 2). The above parameters do not allow to compare the properties of systems with a qualitatively different chemical composition. Yet they reflect a relative change in the energy characteristics of the surface oxygen according to variations of the promoter content [30].

**Table 2. The relative intensity of ion currents as a measure of the Me-O (Zr-O) bond strength.**

| Ratio (R) of ion currents or its logarithm (logR) | Alkali-earth cation content (at. %) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Ca | | | Sr | | | Ba | | |
| | 5 | 10 | 25 | 2 | 5 | 10 | 5 | 10 | 25 |
| $R(ZrO^+/ Zr^+)$ | 0.87 | 0.80 | 0.67 | 0.72 | 0.72 | 0.72 | 0.61 | 0.65 | 0.80 |
| $\log R(MeO^+/Me^+)$ | -2.1 | -2.8 | -3.2 | -1.7 | -0.65 | -2.2 | -1.4 | -1.5 | -1.7 |

Generally, the Zr-O bond energy depends on two factors affecting the bond length: (i) variation of Zr-O coordination number; (ii) deformation of the Zr-O coordination polyhedron, without changing the coordination number (structure relaxation). In the latter case, the shorter the bond length, the higher is its strength. A mean Zr-O bond energy has been found to monotonously increase with the MeO content only for Ba-$ZrO_2$ system, where no reconstruction of the surface layer occurs. In this case, a bulky Ba cation pushes the surrounding anions aside, thereby reducing the distance between them and Zr cations and enhancing the Zr-O bond strength. An opposite situation occurs with the Ca-PSZ system: oxygen anions are drawn around the relatively small Ca cation, stretching the Zr-O distance in neighbouring polyhedrons and lowering the strength of this bond. An intermediate pattern was observed for the Sr-stabilized samples.

A comparison of the data provided in Tables 1 and 2 allows the explanation of the revealed kinetic features. The surface layer reconstruction, which leads to the disappearance of anion vacancies and coordinately unsaturated surface cations, proceeds most easily for Ca-$ZrO_2$ [30]. In addition, the mean Zr-O bond energy declines with the calcium content, due to the surface layer relaxation which should cause a strength decrease of the nitrate bond. As a result, the reaction activation energy decreases, while the low-temperature activity increases. Hence, for this system, at relatively low temperatures, the mean Zr-O bond energy is more important for the catalysis than the number of coordinately unsaturated surface cations. At the same time, the high-temperature activity decreases with the Ca content, due to the reduced surface coverage by the key intermediates: nitrate complexes. Another trend is observed for the Ba-PSZ system, where the surface layer reconstruction does not occur. Here, the activation energy is actually constant and the reaction rate increases with the Ba content, correlating with the number of surface oxygen vacancies. The Sr-PSZ system shows a more complex behaviour: with an increasing Sr content, activity grows at first and then drops. These traits are consistent with the intermediary surface layer restructuring trend inherent to the discussed system.

It is unlikely that the process of hydrocarbon activation on the examined oxides limits SCR of nitrogen oxides, at least, at relatively low GHSV. This conclusion becomes obvious when comparing catalyst specific activity sequences in the reaction of nitrogen oxide selective reduction and deep oxidation (combustion) (Fig. 3 and 4). At close specific rates of butane combustion, activity of $Al_2O_3$ and zirconium oxides in SCR reactions considerably differs. For these systems, a step of the nitrite-nitrate complex formation is likely to be limiting the overall rate of the process. It should be noted that the rate of this step largely depends on the nature of coordinately unsaturated surface sites and their concentration [29, 33].

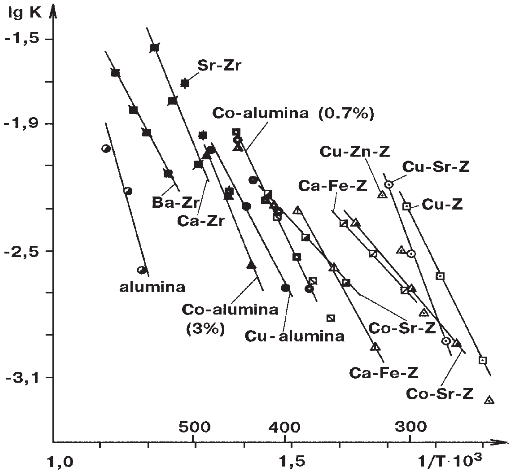

**Fig. 3. Temperature dependences of first-order effective constants for SCR of nitrogen oxides by propane for different-type catalysts. The legends and standard reaction mixture composition are the same as in Fig. 1 - 2.**

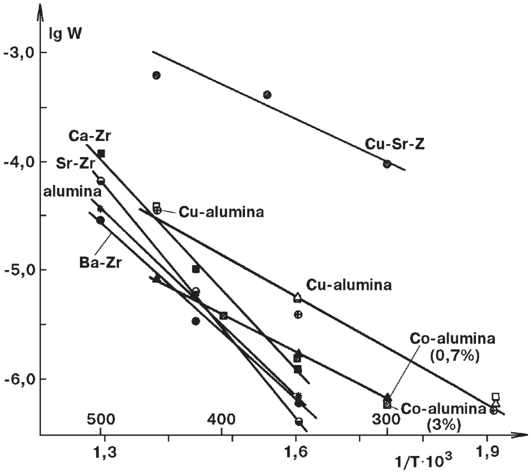

**Fig. 4. Temperature dependence of the specific rates of butane combustion ($cm^3/m^2$ min) in a flow-circulation installation (0.2% mixture in air) for different type catalysts.**

### 2.1.2. Clustering of transition metal cations and the real structure of the active component on the support

For transition metal cations supported onto $Al_2O_3$ and $ZrO_2$ [29, 33, 35, 38-40] or exchanged into zeolites [15, 23, 24, 28], the operational range of SCR-HC is shifted to lower temperatures, when compared with pure supports (Figs. 1 and 3-5). This phenomenon is definitely associated with easier activation of hydrocarbons (Fig. 4), performed via a more effective oxidation route leading to formation of radicals or selective oxidation products, thanks to participation of oxygen bound with transition metal cations [15, 19, 22, 23, 29, 33]. On the other hand, the higher low-temperature efficiency of $NO_x$ SCR-HC, catalyzed by supported transition metal cations, correlates with a lower bonding strength and, hence, with higher reactivity of nitrite-nitrate complexes [12, 15, 22, 33]. For such systems, the active site certainly is a transition metal cation. Reactivity of the surface species bound with those cations is determined by their first coordination sphere, determined by support features, as well as by clustering degree of cations on a given support.

As a rule, comparing $Al_2O_3$ with other mentioned supports, cations of transition metals display noticeable activity at higher temperatures. In addition, higher $NO_x$ conversion degrees are achieved. For Cu and Ni cation, the activity maximum shifts to the low-temperature region along with their loading [29, 33, 38, 40]. An increase in the transition metal cation content on the surface of support favours their clustering, leading to formation of nanoparticles of dispersed oxides.

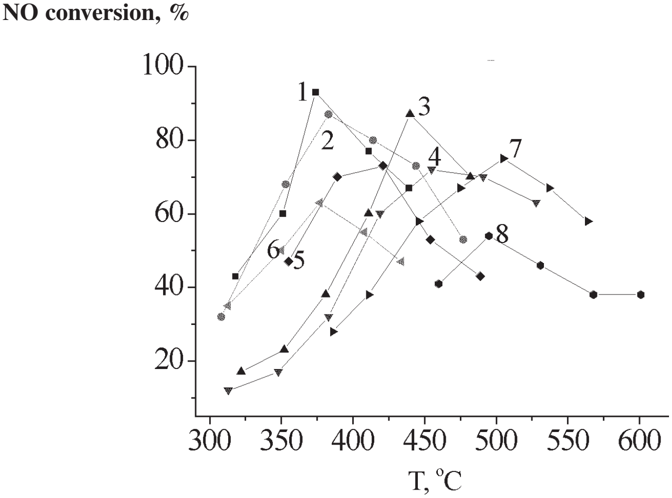

**Fig. 5. Temperature dependence of NO conversion to $N_2$ on the $CuO/Al_2O_3$-$ZrO_2$ (curves 1- 6) and $CuO/Al_2O_3$ samples (curves 7 - 8). Content of Cu (weight %): 1 (curves 7 - 8); 2 (curves 1- 4, 6); 4 (curve 5). GHSV (gas hourly space velocity)- 13,000/h (curves 5 and 8) and 4,000/h in all the other cases. Content of $Al_2O_3$ in $ZrO_2$ (weight %): 1 (curve 1), 2 (curves 5, 3,4,5); 6 (curve 10).**

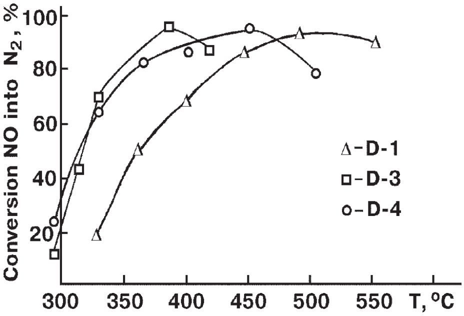

**Fig. 6. Influence of Cu content in the Sr-Cu-ZSM-5 catalyst on NOx conversion during SCR by propane with a standard composition of the reaction mixture. Content of Cu (weight %): 1 (D-1), 2 (D-3) and 5 (D-4).**

The related increase in the rate of the side reaction of deep oxidation results in a decline in the reductant content in the catalyst layer, thus decreasing $NO_x$ conversion. Bulk transition metal oxides, which are good catalysts for deep oxidation reactions, are well known to be poor $NO_x$ SCR-HC catalysts (see reviews [1-9]). However, for Co-supported alumina, even at low loadings, [34], the rate of $NO_x$ reduction declines with Co content (Fig 3), whereas the deep oxidation rate is constant (Fig 4). Similar phenomena were observed for some Co-exchanged ZSM-5 samples [34]. All these features are evidently associated with the structural specifics of transition metal cation clusters on the surface of various substrates, which depends both on the cation nature and on the support surface structure.

Transition metal cation clustering on the surface of $Al_2O_3$- and $ZrO_2$-based supports was examined for copper, nickel, and cobalt oxide systems.

A detailed analysis of the copper oxide system (CO) supported on $Al_2O_3$ and $ZrO_2$ – using different techniques like TEM, XPS, Diffuse Reflectance Electron Spectroscopy (DRS), EPR, IRS of the adsorbed CO test molecule – made it possible to identify a few types of sites on the surface of oxide supports [53, 54]. Those are: isolated copper cations ($Cu^{2+}$); two-dimensional (2D) clusters localized on the most developed $Al_2O_3$ faces of the (110) type; three-dimensional (3D) NaCl-type clusters localized on weakly manifested (100)-faces of $Al_2O_3$, on its surface steps, and on more developed (111)-faces of cubic $ZrO_2$. The concentration of isolated cations is very low (less than several percents of the monolayer). It drops fast as the active component concentration grows. These sites are likely to be copper cations ($Cu^{2+}$) incorporated into cation vacancies on the support surface. According to the EPR data [54], they have a square planar or distorted octahedron coordination. Copper cations are normally present on the $\gamma$-$Al_2O_3$ surface in the form of 2D clusters, covering a larger part of the spinel support surface mostly represented by (110) faces. As follows from the structure of these faces, $Cu^{2+}$ cations incorporated in such clusters are coordinated by four oxygen atoms of the support in the surface plane, one oxygen atom in the subsurface position and one strongly adsorbed bridging oxygen atom. As a result, such copper cations are coordinately saturated and are unable to retain CO even at the liquid nitrogen temperature. It is only possible to eliminate such oxygen using high-temperature evacuation or reduction in CO. The oxygen removal is accompanied by formation of coordinately unsaturated (cus) $Cu^{1+}$ cations capable of retaining CO even at room temperature. According to the EXAFS data [15], a similar local structure of clusters is also specific for over-exchanged Cu-ZSM-5 samples. There is however a meaningful difference. For copper-substituted zeolites, all oxygen atoms in equatorial positions of clusters are of the so- called “extra-lattice type”, i.e. not belonging to the zeolite lattice. They can be rather easily removed by $H_2$ reduction with the formation of metallic Cu although this process occurs less readily than reduction of isolated cations or three-dimensional oxide clusters. Copper oxide clusters on the $Al_2O_3$ surface include copper cations incorporated into cation vacancies of the support, so the extra-lattice oxygen content is considerably less. In principle, this implies both higher stability of the 1+ oxidation state of copper and a higher average strength of the oxygen bond in the Cu coordination sphere. Even for the extra-lattice bridging oxygen, the binding energy is ~70 kJ/mol higher in the case of $Al_2O_3$-supported clusters [15, 54]. The thermal stability of bridging nitrate complexes localized on such clusters usually correlates with the Cu-O bond strength. Thus, at equal heating rates, the $T_{max}$ of $NO_x$ peak is equal to ~400°C for Cu-ZSM-5 and ~480°C for $CuO/Al_2O_3$ [15, 16].

Of maximum interest among the oxide support surface structures are three-dimensional clusters of copper cations. They are precursors of the copper oxide phase. Their specific feature is an easy loss of oxygen under vacuum pretreatment or under the CO action using very low temperatures, comparable to that of liquid nitrogen [53, 54]. For $Al_2O_3$, the concentration of such clusters is not high, and the overall number of associated surface sites does not exceed a few percents of the monolayer, whereas for bulk fluorite-like supports ($ZrO_2$) a larger portion of copper cations is incorporated in these clusters. The easiness of their reduction is primarily determined by their metastable structure (probably of the NaCl type). It enables formation of Cu-Cu bonds during oxygen elimination, facilitating its further removal. The easy reduction of such structures correlates well with the low bonding strength of nitrate complexes ($T_{max}$ of desorption ~380°C [54].

In the case of copper cations supported on ZSM-5 [15, 23, 28], $Al_2O_3$ or $ZrO_2$ [33, 34, 35, 48, 49], the catalytic activity in $NO_x$ SCR by propane at mean temperature (~350°C) increases with the content of the active component (Fig. 6), until the copper oxide phase is formed (loading not exceeding 5% in weight of copper). Both stabilization sites of nitrate complexes and sites of hydrocarbons activation are important in this reaction. In copper-substituted zeolites, 2D clusters perform both functions [15]. In the copper oxide-alumina system, separation of these functions between clusters of different types is possible: two-dimensional clusters stabilize nitrate complexes while three-dimensional clusters predominantly activate hydrocarbons. Such 3D clusters are characterized by a high coordination unsaturation degree even in the presence of gas-phase oxygen and stabilize weakly bound oxygen. The concentration of clusters of both 2D and 3D types grows with the increasing active component concentration, the same happens for the specific catalytic activity in the $NO_x$ SCR by propane. A low strength of the oxygen bond with three-dimensional copper oxide clusters clearly correlates with lower temperatures of the effective action of copper cations on the $ZrO_2$ surface (the temperature of the conversion maximum for nitrogen oxides ~300-350°C), when compared to the copper oxide-alumina system (the temperature of the conversion maximum for nitrogen oxides varies over ~500-600°C depending on the composition of the reaction mixture, Fig. 6). In this respect, Cu-$ZrO_2$ and Cu-ZSM-5 systems are close in efficiency [33, 35]. At the same time, specific catalytic activity of copper cations on the alumina support is considerably overcome by activity of copper cations in zeolites (see also [15, 33]), both in nitrogen oxide SCR (Fig.

3) and in reactions of hydrocarbon full oxidation by molecular oxygen (Fig. 4). Considering the close activation energies in both reactions for copper cations on different supports (Fig. 3 and 4), one may assume that the difference in efficiency basically derives from a much larger portion of coordinately unsaturated copper cations. Differently from the extended two-dimensional clusters on $Al_2O_3$, in this case such cations are gathered in smaller clusters located in zeolite channels.

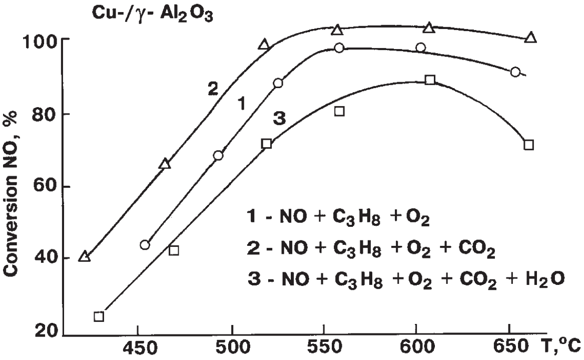

**Fig. 7. Influence of the $CO_2$ (10 %) and water (3%) addition to the standard reaction mixture on the $NO_x$ conversion degree in the course of SCR.**

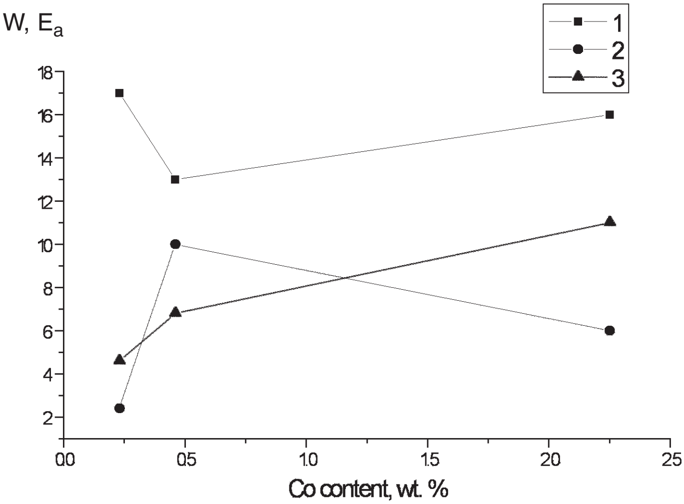

**Fig. 8. Energy of activation $E_a$ (kcal/mol) - 1; specific rate of NO SCR by methane at (1) 210°C ([W] = $10^{11}$ NO molecules/$m^2$s) and (2) 400°C ([W] = $10^{13}$ NO molecules/$m^2$s) - 3 versus Co concentration in Co-ZSM-5.**

A specific feature of copper cations fixed on $ZrO_2$ nanoparticles in pillared clays [38-41, 44] is their ability to penetrate the surface, thanks to loose structure of the nanoparticles. As a result, the tendency to form three-dimensional copper oxide clusters is much weaker than in bulk fluorite-like systems. This is reflected in a dramatically higher average strength of the oxygen bond and its lower reactivity in activation of hydrocarbons. Higher coordinative saturation of copper cations leads to dominating adsorption of nitrogen oxides in the form of nitrite complexes, readily desorbing at temperatures below 250°C [41]. A low surface coverage by these key intermediates suppresses the SCR route at higher temperatures, when the rate of propane activation becomes noticeable. Thus, copper content being the same, activity of copper cations on the surface of bulk $ZrO_2$ in $NO_x$ SCR by propane considerably exceeds activity of copper cations embedded in $ZrO_2$ nanoparticles of pillared clays.

The support nature influences the catalytic properties of copper cations in nitrogen oxide SCR by propylene in oxygen excess in a similar manner [29].

In SCR of nitrogen oxides by propane [15, 34] and methane [15], specific catalytic activity of cobalt cations in ZSM-5 increases along with the Co content (see, e.g. Fig. 8), at temperatures around 400°C. According to the EXAFS data [15], chains of tetrahedrally-coordinated cobalt cations are most probable structures of cobalt oxide clusters in zeolites, with a relatively low Si/Al module ~17 and a cobalt cation content below 2% wt. In this case, the portion of marginal coordinately unsaturated cobalt cations, on which nitrite-nitrate complexes can be localized, is rather large and slightly decreases as the cobalt content grows. However, at lower temperatures (210°C), specific catalytic activity in the reaction of NOx SCR by methane diminishes when the content of the active component exceeds 0.5 % wt. (Fig. 8). This is explained by the fact that the portion of bidentate and bridging nitrate complexes – strongly bound and less reactive – increases with the Co content, while the one of the monodentate nitrate complexes – more reactive at low temperatures – decreases [22]. At a higher zeolite module ~25, the excessive aggregation of cobalt cations in the samples leads to a specific activity decline in $NO_x$ SCR by propane at all temperatures [34].

For alumina-supported Co cations, the increase of their loading from 0.7 to 3% results in a dramatic drop of specific catalytic activity in $NO_x$ SCR by propane (Fig. 3), despite the constant rate of hydrocarbon activation in the presence of molecular oxygen (Fig. 4). Therefore, it is possible to exclude such a trivial reason for the activity decline in the target reaction, as the dominating route of hydrocarbon full oxidation by molecular oxygen. Similar regularities for Co-alumina system were revealed by Yan et al. [56]. Based upon DRS data on Co cations coordination in their samples, these authors assigned active sites of propylene $NO_2$ SCR to octa-coordinated cobalt cations. $CoO_x$ surface clusters were suggested to catalyze full oxidation of hydrocarbons, while inactive tetra-coordinated cations are incorporated into the subsurface layer. Nevertheless, it is evident that such assumption does not explain the hampering of the hydrocarbon oxidation rate when the Co content is higher and, hence, the size of $CoO_x$ clusters is larger. In addition, the authors [56] observed a rise both in activity and selectivity of propylene consumption for nitrogen oxide reduction after annealing of samples at high-temperature (800°C). According to their data, an increase in the concentration of tetra-coordinated cobalt cations occurs. Activity in full hydrocarbon oxidation by molecular oxygen is more likely to be determined by small clusters of tetra- and octa-coordinated cations on (111)- and (100)-faces, respectively, which appears at the lowest concentrations of active component. This may be confirmed by the fact that the strength of the oxygen bond with such clusters is minimal, with respect to all other types of cobalt cation structures on the substrate. Another factor must be considered in order to explain the activity drop in SCR associated with a big surface coverage by cobalt cations. We must consider the SCR reaction mechanism specifics in cobalt oxide systems, where hydrocarbon is activated directly on nitrite-nitrate complexes in the presence of nitrogen oxide [15]. As isolated cations are capable of coordinating nitrite and monodentate nitrate complexes, it is probable that catalytic activity in $NO_x$ SCR by propane on the alumina-cobalt oxide system is determined by such strongly bound intermediates. The situation is different for cobalt cations on $Al_2O_3$ and ZSM-5. In the latter case, activity in the close temperature region depends on bidentate nitrate complexes [15, 22]. A difference in the nature of most active forms of strongly bound intermediate complexes for these two support types is primarily caused by an increased strength of the Co-O bond in cobalt oxide-alumina systems, due to the predominant coordination of the cation by anions of the support. As a result, bidentate nitrate complexes localized on $CoO_x$ spinel clusters become strongly bound and low-reactive in the temperature range below 500°C. At the same time, the increase of the bonding strength of nitrite and monodentate nitrate complexes makes them more stable over the reaction temperature range. This assumption agrees with the results of Yan et al [56], demonstrating stability under the reaction conditions of nitrite-nitrate complexes stabilized on cobalt cations.

Hence, the difference in the nature of SCR active sites supported on $Al_2O_3$ copper oxidic species (clusters of two types) and cobalt oxidic species (mostly isolated tetra-coordinated cobalt cations) originates from the differences both in the metal-oxygen bond strength and in reaction mechanisms. The matrix also plays an important role as it affects the strength of oxygen bonds with copper and cobalt cations and, as a consequence, the bond strength and reactivity of nitrite-nitrate complexes.

Detailed studies on nickel cations on the $ZrO_2$ surface [29, 38, 40] showed that isolated nickel cations (apparently embedded in support surface vacancies) are very active and selective in reactions of $NO_x$ SCR by propylene. Due to a rather high strength of the oxygen bond with such cations, the maximum rate of $NO_x$ reduction shifts towards high temperatures (around 400°C). Clustered octa-coordinated cations-precursors of the nickel oxide phase are able to perform catalysis at lower temperatures, due to the greater reactivity of the related oxygen. However, the highest rate of NO conversion in this case is lower because of intensive propylene combustion.

## 2.2. CONTROL OF THE PROPERTIES OF $NO_X$ SCR-HC CATALYSTS CONTAINING TRANSITION METAL BY ADDITION OF PROMOTERS

### 2.2.1. Oxide additives

Benefits of this approach were firstly demonstrated in some publications of Japanese scientists [57]: the addition of alkali-earth and rare-earth metal cations to zeolites containing cations of transition metals allowed to considerably extend the working temperature range and improve selectivity of the hydrocarbon consumption for $NO_x$ reduction. This was presumed to occur due to a simple suppression of the route of full hydrocarbon oxidation by molecular oxygen [57, 58]. However, these effects can also be caused by stabilizing SCR route intermediates, including nitrite-nitrate complexes and their reductive transformation products containing N and C atoms. This hypothesis has not been properly verified in the available publications.

A positive effect of promoters is also related to the zeolite dealumination suppression in the presence of water vapours at elevated temperatures. Dealumination is known to cause an activity loss, due to the destabilization of transition metal cations and their segregation with formation of oxide particles. An important issue is the concentration of protons bound with Broensted acid sites responsible for dealumination [58], which is fundamental for copper-exchanged zeolites. The problem of dealumination is less significant for cobalt-exchanged zeolites, because cobalt cations themselves drastically improve hydrothermal stability of ZSM-5 [59]. Yet the addition of lanthanum cations [60] enhances hydrothermal stability and activity of cobalt-exchanged zeolites as well.

Any design of commercial catalysts based on cation-exchanged zeolites should take into account the influence of a binder. It is used either in the course of zeolite washcoating on ceramic or metal monolithic substrates with suspensions and during extrusion of bulk samples in the form of granules or monoliths. Aluminium hydroxide peptized in acidic solutions was most often utilized as a binding agent. However, the use of such a binder for zeolite catalysts leads to their deactivation caused by the migration of aluminium cations to zeolite channels and the neutralization of Broensted acid sites or formation of Lewis sites [61]. Evidently this factor is one of the reasons for the dramatic decline in activity of monolithic catalysts based on copper-exchanged zeolites, if compared to zeolite powder. It is clear that such effects should be considered in the promoter selection and introduction to $NO_x$ SCR catalysts based on cation-exchanged zeolites.

Based upon determining role of nitrite-nitrate complexes in the SCR-HC reaction route, it was assumed that their stabilization on the surface at elevated temperatures can be ensured by adding cations of alkali-earth metals and zinc to assure their high activity at large space velocities. This assumption was shown to be true for three types of transition metal cations: Cu, Co, and Fe. A comparison of the data on TPD of nitrogen oxides [12, 15, 24, 25] shows that the introduction of alkali-earth metal cations does not actually change the position of the thermal desorption peak, which corresponds to the decomposition of nitrate complexes. Instead, it increases several folds the surface coverage. This may imply either that bond strengths of nitrate complexes with transition metal cations and promoters are comparable, or that nitrate complexes on these two types of sites are in equilibrium with each other, at least, at elevated temperatures.

When nitrogen oxide is not present in the gas phase, the rate of hydrocarbon oxidation by molecular oxygen almost does not change with the addition of promoters such as Sr and Zn. This implies that neither blocking of transition metal cations by promoting cations nor any detectable change in the strength of the oxygen bonding with the active sites occurs. These results disprove the issue of a simple suppression of the deep oxidation route by those promoters [57].

For better understanding of the nature of promoter influence, it is important to consider that, in the case of Cu- and Co-substituted zeolites, a certain increase in the effective energy of the SCR reaction is observed, along with a decrease in activity at low-temperatures (200 - 300°C), when base cations (Zn, Ca, Sr) are added (Fig. 3).

In this temperature range, activity of non-modified samples also depends, to a great extent, on the surface coverage by nitrite complexes stabilized on isolated cations of transition metals. For such less strongly bound species, the SCR reaction proceeds with a high efficiency due to a lower activation energy [15]. This suggests that addition of base promoters helps to convert nitrites into more strongly bound bidentate or bridged nitrates, which are stabilized on two types of cations. The comparison of the TPD data for Cu-ZSM-5 and Co-ZSM-5 [12, 15, 24, 25, 57, 63] reveals that the addition of the Sr cation indeed leads to decline of the low-temperature shoulder on the high-temperature peak of the $NO_x$ release. This change is likely to be caused by the reduction of the surface coverage by nitrate complexes bound to isolated Cu and Co cations.

There obviously exist other factors in addition to the discussed mechanism of the modifying cation influence on activity and selectivity of zeolites containing transition metal cations. First, promoter cations themselves are able to stabilize mono- or bidentate nitrite-nitrate complexes, that may be responsible for catalytic activity in that or another temperature region. For example, when iron cations were introduced to the Fe-ZSM-5 lattice during the hydrothermal synthesis, the TPD spectrum [12, 25] showed that strong adsorption forms of nitrogen oxides were merely represented by nitrite complexes decomposing with the $NO_2$ release. The Ca addition does not induce appearance of bidentate nitrate complexes stabilized on a pair of different-type cations. This suggests that the working temperature range expansion for this system is primarily related to the emergence of nitrite complexes, adsorbed on calcium cations, being more reactive at high temperatures.

Another mechanism of the promoter action is realized when Sr is added to Cu-ZSM-5. In this case, the system manifests activity in $NO_x$ SCR by methane [25]. A primary reason for the low stationary selectivity of $CH_4$ consumption for $NO_x$ reduction – in the case of the non-promoted Cu-ZSM-5 sample – could be an inability of copper cations to retain nitromethane and the products of its further transformation. Such molecules (i.e. nitriles and isocyanates as intermediates involved into $NO_x$ SCR route) cannot be maintained in the axial positions of the square-planar-coordinated copper cations [22, 23]. Strontium cations have a higher capacity of retaining $CN^-$ and $NCO^-$ anions than copper cations. Their introduction to the system ensures relative stability, which is needed either for their further smooth interaction with weakly bound reaction mixture components and for the hydrolysis of C,N-containing species yielding ammonia, thus ensuring the nitrogen atoms coupling route.

### 2.2.2. Noble metal additives

The influence of Ag additives on activity in $NO_x$ SCR by propane, propylene and decane was studied for Cu and Co cations spread on mesoporous supports, based on partially stabilized $ZrO_2$ [33, 38. 40]. A significant effect was found only when the preparation technique provided a strong interaction between the metal and oxide components, i.e. formation of mixed clusters. Such an interaction diminishes the bond strength between oxygen and nitrite-nitrate complexes and the superficial sites, thereby enhancing their reactivity. In all three reactions, the activity level at moderate temperatures (250-350°C) approached that of the most efficient Cu-containing systems: Cu-ZSM-5, Cu-sulphated $ZrO_2$, and Cu-β zeolite. In the $NO_x$ SCR by propylene and decane, the surface of supported Cu systems is heavily covered by hydrocarbons. Addition of Ag raises the surface oxidative ability thus preventing its coking.

The influence of Pt additives on activity of copper cations in $NO_x$ SCR by the same three reducers was examined in the systems based on $ZrO_2$-pillared clays [41]. In relation to this combined component and its preparation process (sequential supporting: first copper cations and then Pt), Pt clusters were shown to be predominantly fixed on copper cations, partially shielding them. A strong interaction between metal and oxide components changes the Pt state, which becomes more oxidized. The copper cation fixation on $ZrO_2$ nanoparticles (pillars) contributes to weakening the interaction of Pt with the pillars and prevents its penetration into $ZrO_2$ nanoparticles. The Pt interaction with copper cations affects its capacity of hydrocarbon activation. The result is the slowing down of propane oxidation by molecular oxygen at its low concentration in $NO_x$-free mixtures. However, the mixed Pt+CuOx clusters are significantly less sensitive to the negative effect of combined $O_2$ and NO on the propane oxidation rate than the pure components. An increase in the Pt oxidation degree lowers the bonding strength of nitrosyls and facilitates their oxidation to reactive nitrite complexes migrating to neighboring cations $Cu^{2+}$ and $Zr^{4+}$.

Activation of hydrocarbons on Pt atoms – followed by the interaction of activated hydrocarbon fragments with nitrite-nitrate complexes localized on the copper cation at the boundary with Pt clusters – is the reason for the elevated low-temperature activity of the combined active component localized on $ZrO_2$ nanoparticles in pillared clays.

The use of the combined active component in pillared clays, supplemented by modification of $ZrO_2$ pillars by Ce and Fe cations [41, 48, 49], allowed achieving a higher degree of $NO_x$ SCR by decane (Fig. 6). It should be highlighted that these catalysts in real mixtures are characterized by the same high performance in the presence of water and sulphur dioxide.

Propylene is however a more efficient reducer: the nitrogen oxide conversion is higher within a broader temperature range and at higher space velocities (Fig. 10). The combined active component in mixtures having high $O_2$ and $H_2O$ concentrations provides high selectivity for $N_2$ formation (90-95%), selectivity for $N_2O$ (an undesirable by-product) formation being minimal (5-10%). At the same time, selectivity for $N_2O$ reached 30% in dry mixtures with a small oxygen excess (1 - 2%).

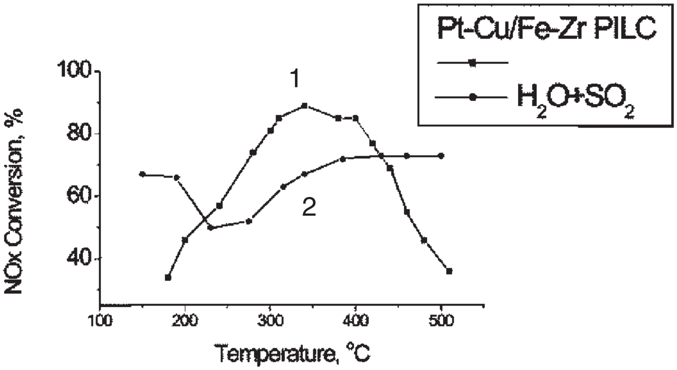

**Fig. 9. Temperature dependence of the $NO_x$ conversion degree on the catalyst based on $ZrO_2$-pillared montmorillonite clay (Fe-Zr PILC) with the mixed (Pt-Cu) active component in NO SCR by decane in the dry feed 0.15% NO and 0.05% decane in air (1) and in the feed with addition of 3% water and 0.03% $SO_2$ additives to the mixture (2).**

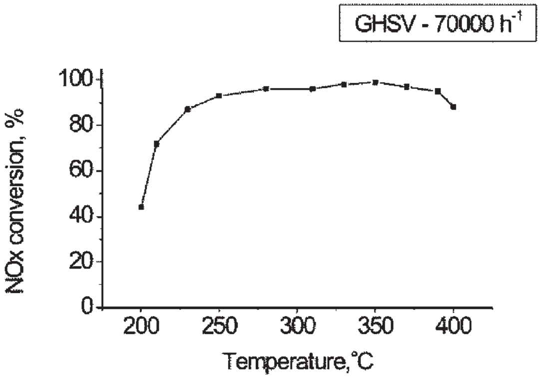

**Fig. 10. Temperature dependence of the $NO_x$ conversion degree on the catalyst based on $ZrO_2$-pillared montmorillonite clay (Fe-Zr PILC) with the mixed (Pt-Cu) active component in NO SCR by propylene. Composition: 0.15% NO, 0.14% $C_3H_6$, 1% $O_2$, 3 % water and 0.03% $SO_2$; feed space velocity 70,000/h.**

### 2.2.3. Combined layers of different catalysts

As catalysts based on Pt and pillared clays are active at low temperatures, while the ones based on bulk $ZrO_2$ – at high-temperatures, it appeared promising to try combinations of these types of catalysts in successive layers [48]. Using a front-layer with a high-temperature catalyst led to a considerable extension of the temperature region of effective $NO_x$ abatement during $NO_x$ SCR by propylene in $O_2$ excess (Fig. 11).

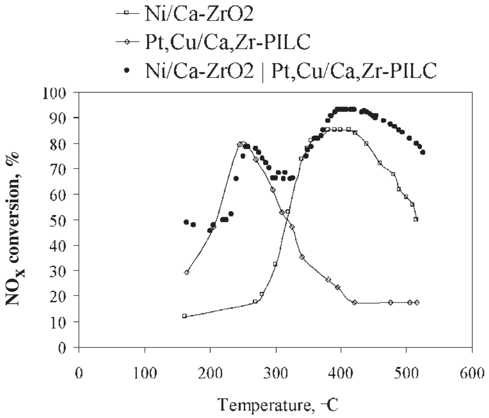

**Fig. 11. Influence of combining of two types of active components in the catalytic layer on nitrogen oxides conversion in the course of SCR by propylene in $O_2$ excess (29). Reaction mixture: 0.2% NO+0.2% $C_3H_6$+ 2.5% $O_2$; space velocity 9,000 $h^{-1}$.**

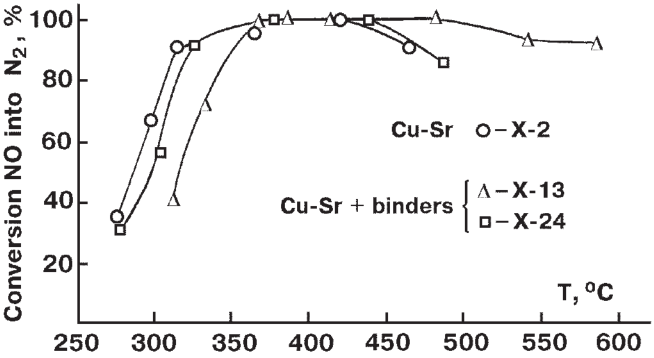

**Fig. 12. Influence of a binder on activity of the Cu-ZSM-5 catalyst modified by Sr in $NO_x$ SCR by propane. Standard reaction mixture, space velocity 4,000 $h^{-1}$.**

### 2.2.4. Influence of a binder

A binder based on alumosilicates [27, 28] was selected for the promoted samples of cation-exchanged zeolites. It allowed the preparation of granules and bulk monolithic catalysts retaining a high performance level (Fig. 12). A distinctive feature of such systems is high $NO_x$ conversion at large space velocities in real mixtures, characterized by high concentrations of $H_2O$ and $SO_2$, two typical poisons for this reaction (Fig. 13). The NOx conversion degree is not space-time dependent using the catalysts tested in the form of fractions in the fixed bed layer. That most probably relates to less steep concentration profile of the reductant (propane) in the layer at high GHSV, which helps to achieve more efficient reduction of nitrogen oxides.

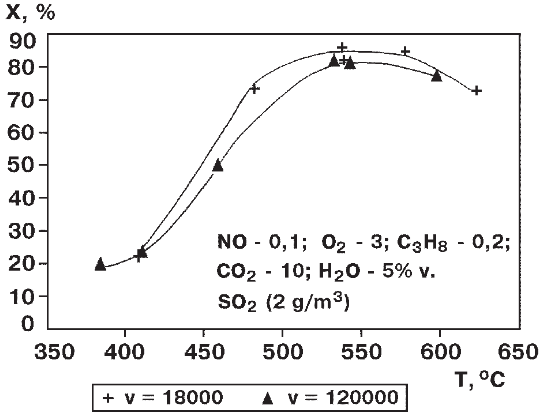

**Fig. 13. Influence of the load on $NO_x$ conversion under SCR by propane in $O_2$ excess with close-to-real compositions of the reaction mixture. The catalysts Cu-ZSM-5 modified by Sr was shaped into monoliths with a binder and tested in the form of a 0.5-1 mm fraction.**

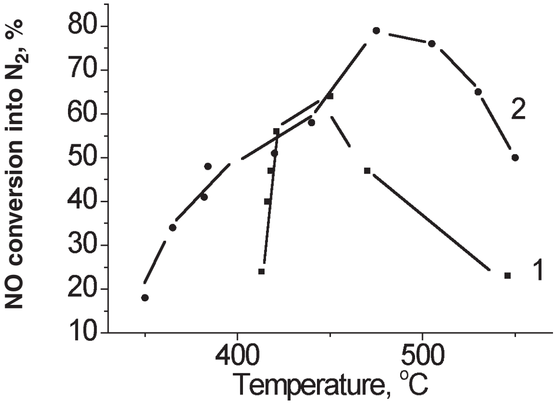

**Fig. 14. Influence of Pd on the operational efficiency of monolithic catalysts based on Co-substituted ZSM-5. Tests in the 0.5-1 mm fraction form; reaction mixture: 0.02% NO, 0.4 % $CH_4$, 16% $O_2$, and 2% $H_2O$; space velocity 12,000/h. 1- initial catalyst; 2- catalyst promoted by 0.2% wt. Pd**

It is apparent that such an effect can be observed only in the case of a very high rate of propane activation in realistic feeds. In our case, it is ensured by a rather high content of the active component (2-5% wt.) in the catalyst leading to strong clustering of copper cations. For methane, a less reactive reductant, with humid feeds its activation on nitrate complexes bound with cobalt cations does not apparently proceed fast enough (Fig. 14), leading to a lower level of $NO_x$ conversion and a much narrower operating temperature range. Promotion of the catalyst by a small amount of Pd - known to be very efficient in methane activation - indeed helped to enhance performance and extend the operation temperature range.

Zeolite-containing components based on the Cu-Sr/ZSM-5 system – additionally promoted by Pd – were supported on thin-walled monolithic substrates made of anodic-spark oxidized and thermally stabilized aluminium foil [63]. Such catalysts, together with monolithic catalysts designated for removing liquid particulates, carbon monoxide and hydrocarbons were tested in a diesel exhaust converter of a city bus Ikarus. The tests proved successful: the nitrogen oxide elimination level of minimum 50% was sustainable during at least four months.

A procedure for supporting the systems based on pillared clays and zirconium framework phosphates, containing Pt-promoted copper cations on cordierite thin-walled monoliths with the density of 400 cells per square inch, has been developed. Suspensions of the active component with binder based on aluminium hydroxide or zirconium oxonitrate were used for their preparation [49, 51]. In SCR of $NO_x$ by decane in $O_2$ excess, even in mixtures with a high water content, on micromonolithic pieces tested in a flow reactor, high nitrogen oxide and decane conversions are reached (Figs. 15 and 16). They can compete with the best results attained on supported Pt catalysts designed by Mazda Motor [64, 65]. A combination of Pt, Rh and Ir introduced into H-ZSM-5 supported on cordierite monoliths is employed in the above catalysts. With the $CeO_2$ additive, the nitrogen oxide conversion reaches 70% in FTP tests. However, ageing of the catalysts operated under stringent conditions diminished performances. This was probably due to the thermodynamic instability of the zeolite structure. None of such features was identified in the operation of our catalysts

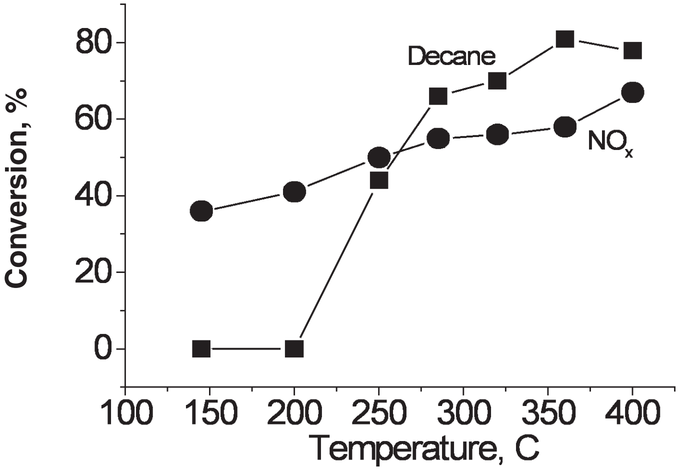

**Fig. 15. Temperature dependences of decane and nitrogen oxides conversion over micromonolith catalyst (Pt-Cu/Zr PILC/cordierite, alumosilicate-based binder). Composition: 0.05% decane, 0.1% NO, 10% $H_2O$ and 10 % $O_2$ in He. Space velocity 25,000 $h^{-1}$.**

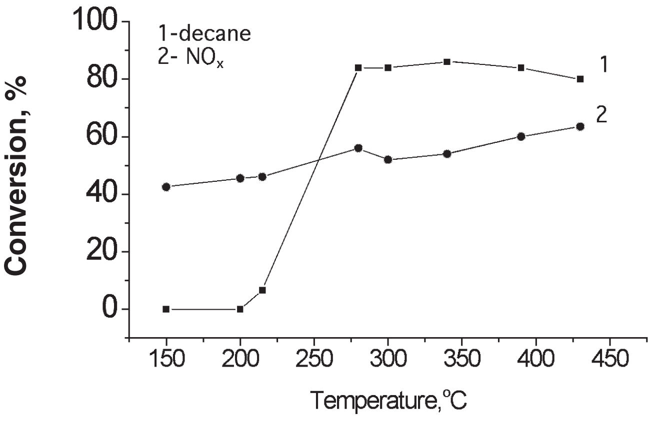

**Fig. 16. Temperature dependences of decane and nitrogen oxides conversion over micromonolith catalyst Pt+Cu - zirconium phosphate/cordierite ($ZrO_2$-based binder) in $NO_x$ SCR by decane. Feedstock composition: 0.05% decane, 0.1% NO, 10% $H_2O$ and 10 % $O_2$ in He. Space velocity 30,000 $h^{-1}$.**

## CONCLUSION

Identification of the basic characteristics of the mechanism of nitrogen oxide SCR by hydrocarbons in oxygen excess allowed us to approach the solution of the catalyst design problem for such processes.

The primary requirement to the active component is a combination of two functions. The first is a sufficient bond strength of the key intermediates, i.e. nitrite-nitrate complexes, with surface active sites and, consequently, attainment of sufficiently high coverage by those species under real catalytic conditions. The second is a high rate of the hydrocarbon activation on such centres and efficient interaction of activated fragments with nitrite-nitrate complexes.

The properties of active sites are controlled by changing their chemical nature (the type of transition metal cation on the support surface) and the coordination environment (governed by properties of the support/matrix, as well as by the clustering degree of cations on the support). Approaches based on the distribution of functions appear to be the most efficient; here nitrite-nitrate complexes stabilization and hydrocarbon activation are respectively due to oxide and metal constituents of the nano-structured active component.

The above criteria were applied to active components based on Cu, Co, Ni and Fe cations, including those promoted by Ag or Pt, and fixed on supports such as high-silica zeolites, partially stabilized $ZrO_2$, and natural clays pillared by $ZrO_2$. Such approach allowed design of systems with a high activity and selectivity for the target reactions, with off-gas compositions being close to realistic ones, facilitating their practical application. We developed methods for supporting these active components on honeycomb monolithic substrates or extruding of monoliths, including active components combined with various binders. The catalysts are covered by patents of the Russian Federation.

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## REFERENCES

1. M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno. Shokubai (Catalyst), 1990, v. 32, pp. 430-433.
2. M.Iwamoto. Proc. Meeting of Catalyt. Technol. for Removal of Nitrogen Monoxide, Tokyo, 1990, p. 1
3. W.Held, A.Koenig, Ger. Offen., DE 3 642 018 (1987).
4. W.Held., A.Koenig, T.Richter, L.Puppe. SAE Paper 900496 (1990).
5. M.Iwamoto, N.Mizuno; H.Yahiro. In: New Frontiers in Catalysis (Proc. 10th Int. Congr. Catalysis), Akademiai Kiado, Budapest, 1993, part. B, p. 1285.

6. M. Iwamoto. In: Zeolites and Related Microporous Materials: State of the Art 1994. (Proc. 10th Int. Zeolite Conf.), J. Weitkamp , H. G. Karge, H. Pfeifer, and H. Holderich, Eds. p. 1395-1410.
7. M. Iwamoto. Catal. Today, 1996, v. 29, No 1-4, p. 29-35.
8. M.D. Amiridis, T. Zhang, R.J.Farrauto. Appl. Catal. B:Environ. 1996, v. 10, p. 203-227.
9. G.Centi, S.Perathoner. Appl. Catal. A, 1995, v. 132, p. 179-259.
10. A.P.Walker. 1995, v. 26, p. 107-128.
11. R.Burch. Catal. Today, 1997, v. 35, p. 27-36.
12. V.A Sadykov, S.L.Baron, V.A.Matyshak, G.M.Alikina, R.V.Bunina, A.Ya.Rozovskii, V.V Lunin, E.V.Lunina, A.N.Kharlanov, A.S.Ivanova, S.A.Veniaminov. Catal. Lett. 1996. V. 37. P. 157.
13. V.A.Matyshak, S.L.Baron, A.A.Ukharskii, A.N.Il'ichev, V.A.Sadykov, V.N.Korchak. Kinetics and Catalysis. 1996. V. 37. P. 549.
14. V.A.Sadykov, E.A.Paukshtis, S.A.Beloshapkin, G.M.Alikina, S.A.Veniaminov, R.V.Bunina, E.V.Lunina, A.N.Kharlanov, V.V.Lunin, V.A.Matyshak, A.Ya.Rozovskii. Proc. 8th Int. Symp. on Heterog. Catalysis. Varna. 1996. V.1. P. 347.
15. V.A.Sadykov, S.A.Beloshapkin, E.A.Paukshtis, G.M.Alikina, D.I.Kochubei, S.P.Degtyarev, N.N.Bulgakov, S.A.Veniaminov, R.V.Bunina, A.N.Kharlanov, E.V.Lunina, V.V.Lunin, V.A.Matyshak, A.Ya.Rozovskii. Pol. J. Environ. Stud. 1997. V. 1. P. 21.
16. V.A.Sadykov, S.A.Beloshapkin, E.A.Paukshtis, G.M.Alikina, D.I.Kochubei, S.P.Degtyarev, N.N.Bulgakov, S.A.Veniaminov, E.V.Netyaga, R.V.Bunina, A.N.Kharlanov, E.V.Lunina, V.V.Lunin, V.A.Matyshak, A.Ya.Rozovskii. React. Kinet. Catal. Lett. 1998. V. 64. P. 185.
17. V.A.Sadykov, A.Ya.Rozovskii, V.V.Lunin, G.I. Lin, G.M.Alikina, G.A.Buchtiyarova, B.P. Zolotovskii, S.A.Beloshapkin. React. Kinet. Catal. Lett. 1999. V. 66. P. 337.
18. S.A.Beloshapkin, V.A.Matyshak, E.A.Paukshtis, V.A.Sadykov, A.N.Ilyichev, A.A.Ukharskii, V.V.Lunin. React. Kinet. Catal. Lett. 1999. V. 66. P. 297.
19. V.A.Matyshak, A.A.Ukharskii, A.N.Ilyichev, V.A.Sadykov, V.N.Korchak. Kinetics and Catalysis. 1999. V.40. P. 116.
20. S.A.Beloshapkin, E.A.Paukshtis, V.A.Sadykov. J. Molec. Catal. A: Chem. 2000, V. 158. P. 355.
21. V.A.Matyshak, A.N.Ilyichev, A.A.Ukharsky, V.N.Korchak. J. Catal. 1997. V. 171. P. 245.
22. V.A.Sadykov, V.V.Lunin, V.A.Matyshak, E.A.Paukshtis, A.Ya.Rozovskii, N.N.Bulgakov, J.Ross. Kinetics and Catalysis. 44 (2003) 412-435.
23. S.A.Beloshapkin. PhD Dissertation. Boreskov Institute of Catalysis SD RAS, Novosibirsk, 2000.
24. V.A.Sadykov, A.Ya.Rozovskii, V.V.Lunin, V.A.Matyshak U.S.-Russia Workshop on Environmental Catalysis. Wilmington, Delaware, 1994. P. 20.
25. V.A.Sadykov, G.M.Alikina, R.V.Bunina, S.L.Baron, S.A.Veniaminov, V.N.Romannikov, Doronin V. P., Rozovskii A. Ya., Tretyakov V. F., V.V.Lunin, E.V.Lunina, A.N.Kharlanov, MatyshakV. A. In: Environmental Catalysis for a better World and Life (Proc. 1st World Congress on Envir. Catal., Pisa, Italy, 1995; G. Centy, C. Cristiani, P. Forzatti, S. Perathoner, Eds.), Societa, Chimica Italiana, Roma, Italy. P. 315.
26. V.A.Sadykov, G.M.Alikina, S.L.Baron, S.A.Veniaminov, R.V.Bunina, E.A.Paukshtis, E.V. Lunina, A.N.Kharlanov, V.V.Lunin, V.A.Matyshak, A.Ya.Rozovskii. Abstr. 11th Intern. Congr. Catal., Baltimore, USA. 1996. Po-202.
27. V.N.Romannikov, G.M.Alikina, V.A.Sadykov, R.V.Bunina, V.V.Lunin, A.Ya.Rozovskii. Catalyst for the process of the nitrogen oxides abatement in the exhausts and method of its preparation. Patent RU No 2072897 (1994).

28. V.A.Sadykov, R.V.Bunina, G.M.Alikina, A.Ya.Rozovskii, V.V.Lunin, V.V.Karpan, S.A.Buymov, V.F.Tretyakov, V.P.Doronin. Method of purification of the exhausts from the nitrogen oxides. Patent RU No 2088316 (1995).
29. G.A.Konin. PhD Dissertation. Semenov Institute of Chemical Physics RAS, Moscow, 2001.
30. V.A.Sadykov, A.S.Ivanova, V.P.Ivanov, G.M.Alikina, A.N.Kharlanov, E.V.Lunina, V.V.Lunin, V.A.Matyshak, N.A.Zubareva, A.Ya.Rozovskii, Mater. Res. Soc. Symp. Ser., v. 454 (Advanced Catalytic Materials), 1997, p. 199-204.
31. A.S.Ivanova, G.M.Alikina, L.P.Solovyova, V.P.Ivanov, S.N.Trukhan, V.A.Sadykov. React. Kinet. Catal. Lett. 1996, Vol. 59, No 1, p. 125-134 ()
32. A.N.Kharlanov, N.A.Zubareva, E.V.Lunina, V.V.Lunin, V.A.Sadykov, A.S.Ivanova. Vestnik MGU, Ser. 2, Khimia, 1998, v. 39, No 1, p. 29-32.
33. V.A.Sadykov, R.V.Bunina, G.M.Alikina, A.S.Ivanova, T.G.Kuznetsova, S.A.Beloshapkin, V.A.Matyshak, G.A.Konin, A.Ya.Rozovskii, V.F.Tretyakov, T.N.Burdeynaya, M.N Davydova, J.R.H.Ross, J.P.Breen. J.Catal. 2001. V.199. P. 131.
34. O.V.Metelkina, V.V.Lunin, V.A.Sadykov, S.A.Beloshapkin, G.M.Alikina, E.V.Lunina, A.N.Kharlanov. Neftekhimia. 2000. V. 40. P. 108
35. O.V.Metelkina, V.V.Lunin, V.A.Sadykov, G.M.Alikina, R.V.Bunina, E.A.Paukshtis, V.B.Fene lonov, A.Yu.Derevyankin, V.I.Zaikovskii, U.Schubert, J.R.H.Ross. Catal. Lett. 2002. V. 78. P. 111.
36. G.A.Konin, A.N.I'ichev, V.A.Matyshak, T.I.Khomenko, V.N.Korchak, D.M.Papakhin, D.Yu.Kuritsyn, A.S.Ivanova, V.A.Sadykov, A.Ya.Rozovskii, J.R.H.Ross. Europacat-V, September, 2001, Limerick, Ireland. Abstracts Book 2. 21-O-10.
37. A.S.Ivanova, G.M.Alikina, V.A.Sadykov, V.V.Lunin, A.Ya.Rozovskii, Yu.S.Khodakov. Catalyst of the reduction of nitrogen oxides by hydrocarbons and method of its preparation. Patent RU No 2043146 (1992).
38. G.A.Konin, A.N.I'ichev, V.A.Matyshak, T.I.Khomenko, V.N.Korchak, V.A.Sadykov, V P. Doronin, R.V.Bunina, G.M.Alikina, T.G.Kuznetsova, E.A.Paukshtis, V.B.Fenelonov, V.I. Zaikovskii, A.S.Ivanova, S.A.Beloshapkin, A.Ya.Rozovskii, V.F.Tretyakov, J.R.H.Ross, J.P.Breen. Topics in Catalysis. 2001. V. 17. No 1-4. P. 193.
39. V.A.Sadykov, R.V.Bunina, G.M.Alikina, V.P.Doronin, T.P.Sorokina, D.I.Kochubei, B.N. Novgorodov, E.A.Paukshtis, V.B.Fenelonov, A.Yu.Derevyankin, A.S.Ivanova, V.I.Zaikovskii, T.G.Kuznetsova, S.A.Beloshapkin, V.N.Kolomiichuk, L.M.Plasova, V.A.Matyshak, A.Konin, A.Ya.Rozovskii, V.F.Tretyakov, T.N.Burdeynaya, M.N.Davydova, J.R.H.Ross, J.P.Breen, F.C.Meunier. Mat. Res. Soc. Symp. Proc., 581, 435-440 (2000).
40. G.A.Konin, A.N.Il'ichev, V.A.Matyshak, T.I.Khomenko, V.N.Korchak, V.A.Sadykov, V P. Doronin, R.V.Bunina, G.M.Alikina, T.G.Kuznetsova, E.A.Paukshtis, V.B.Fenelonov, V.I. Zaikovskii, A.S.Ivanova, S.A.Beloshapkin, A.Ya.Rozovskii, V.F.Tretyakov, J.R.H.Ross, J.P.Breen. Proc. CAPOC-5. Brussels, 2000. V. 2. P. 97.
41. V.A.Sadykov, T.G.Kuznetsova, V.P.Doronin, T.P.Sorokina, G.M.Alikina, D.I.Kochubei, B.N.Novgorodov, E.A.Paukshtis, V.B.Fenelonov, V.I.Zaikovskii, V.A.Rogov, V.F.Anufrienko, N.T.Vasenin, V.A.Matyshak, G.A.Konin, A.Ya.Rozovskii, V.F.Tretyakov, T.N.Burdeynaya, , V.F.Tretyakov, T.N.Burdeynaya, J.P.Breen. Chemistry for Sustainable Development 2003, 11, 249-262.
42. V.A.Sadykov, T.G.Kuznetsova, V.P.Doronin, T.P.Sorokina, D.I.Kochubei, B.N.Novgorodov, V.N.Kolomiichuk, E.M.Moroz, D.A.Zyuzin, E.A.Paukshtis, V.B.Fenelonov, A.Yu.Derevyankin,

S.A.Beloshapkin, V.A.Matyshak, G.A.Konin, J.R.H.Ross. Mat. Res. Soc. Symp. Proc. 2002, V. 703, p. 529.

43. V.B.Fenelonov, A.Yu.Derevyankin, V.A.Sadykov. Microporous Mesoporous Materials, 2001, v. 47, p. 359-368.
44. V.A Sadykov, T.G.Kuznetsova, V.P.Doronin, E.M.Moroz, D.A.Ziuzin, D.I.Kochubei, B.N. Novgorodov, V.N.Kolomiichuk, G.M.Alikina, R.V.Bunina, E.A.Paukshtis, V.B.Fenelonov, A.Yu.Derevyankin, O.B.Lapina, I.Yu.Yudaev, V.A.Matyshak, V.V.Lunin, A.Ya.Rozovskii , V.F.Tretyakov, T.N.Burdeynaya, J.R.H.Ross. Proc. X APAM Topical Seminar and III Conference “Materials of Siberia”, “Nanoscience and Technology”, June 2-6, 2003, Novosibirsk, Russia, p. 208-209.
45. V.A.Sadykov, T.G.Kuznetsova, G.M.Alikina, V.P.Doronin, T.P.Sorokina, R.V.Bunina, D.I.Kochubei, B.N.Novgorodov, E.A.Paukshtis, V.B.Fenelonov, A.Yu.Derevyankin, V.I. Zaikovskii, S.A.Beloshapkin, V.N.Kolomiichuk, V.F.Anufrienko, N.T.Vasenin, A.Ya. Rozovskii, V.F.Tretyakov, T.N.Burdeynaya, M.N.Davydova, V.A.Matyshak, G.A.Konin, J.R.H.Ross, J.P.Breen. Europacat-V, September, 2001. Limerick, Ireland, Abstracts Book 3. 7-O-03.
46. T.G.Kuznetsova, V.A.Sadykov, E.A.Paukshtis, V.A.Matyshak, G.A.Konin, V.A.Rogov, V.P. Doronin, T.P.Sorokina, J.R.H.Ross. VI Conference “Mechanisms of Catalytic Reactions”, October 1-5, 2002, Moscow, Russia, v. 2, p. 197-198.
47. V.A.Sadykov, V.P.Doronin, T.P.Sorokina, T.G.Kuznetsova, G.M.Alikina, R.V.Bunina, D.I.Kochubei, B.N.Novgorodov, E.A.Paukshtis, V.B.Fenelonov, A.Yu.Derevyankin, V.I. Zaikovskii, V.N.Kolomiichuk, V.F.Anufrienko, A.Ya.Rozovskii, V.F.Tretyakov, T.N.Burdeynaya, V.A.Matyshak, G.A.Konin, J.R.H.Ross. In Abstracts, Russian -Dutch Workshop “Catalysis for Sustainable Development”, June 22-25, 2002, Novosibirsk, Russia, P. 235-236.
48. T.G.Kuznetsova, V.A.Sadykov, T.P.Sorokina, V.P.Doronin, G.M.Alikina, R.V.Bunina, A.S. Ivanova, V.A.Matyshak, G.A.Konin, A.Ya.Rozovskii, T.N.Burdeynaya, V.F.Tretyakov, J.R.H.Ross. Catalyst, Catalyst Carrier, their Preparation Technique (Variants) and Technique of Off-Gas Treatment from Nitrogen Oxides (Variants). RF Patent No. 2194573 of 17.09.01.
49. T.G.Kuznetsova, V.A.Sadykov, T.P.Sorokina, V.P.Doronin, G.M.Alikina, R.V.Bunina, A.S. Ivanova, V.A.Matyshak, G.A.Konin, A.Ya.Rozovskii, T.N.Burdeynaya, V.F.Tretyakov, J.R.H.Ross. Catalyst, Catalyst Carrier, their Preparation Technique (Variants) and Technique of Off-Gas Treatment from Nitrogen Oxides (Variants). RF Patent No. 2199389 of 17.09.01.
50. V.A.Sadykov, S.P.Pavlova, M.V.Chaikina, G.V.Zabolotnaya, R.I.Maksimovskaya, S.V.Tsybulya, E.B.Burgina, V.I.Zaikovskii, G.S.Litvak, Yu.V.Frolova, D.I.Kochubei, V.V.Kriventsov, E.A.Paukshtis, V.N.Kolomiichuk, V.P.Ivanov, V.F.Anufrienko, N.N.Boldyreva, N.N.Kuznetsova, V.V.Lunin, D.Agrawal, R.Roy. Chemistry for Sustainable Development, 2002, v. 10, p. 227-235
51. S.N.Pavlova, V.A.Sadykov, G.V.Zabolotnaya, Y.V.Frolova, O.B.Lapina, V.M.Bondareva. Abstr. 3rd Intern. Conf. Inorganic Materials, Konstanz, Germany, 7-10 September 2002, P 179.
52. V.V.Kriventsov, D.I.Kochubey, V.A.Sadykov, S.N.Pavlova, G.V.Zabolotnaya. Nuclear Instruments and Methods in Physics Research 470 (2001), 1-2, pp. 336-340.
53. V.A.Sadykov, R.V.Bunina, G.M.Alikina, A.S.Ivanova, D.I.Kochubei, B.N.Novgorodov, E.A.Paukshtis, V.B.Fenelonov, V.I.Zaikovskii, T.G.Kuznetsova, S.A.Beloshapkin, V.N. Kolomiichuk, E.M.Moroz, V.A.Matyshak, G.A.Konin, A.Ya.Rozovskii, J.R.H.Ross, J.P.Breen. J. Catal. 2001, 200, 117-130.

54. S.F.Tikhov, V.A.Sadykov, G.N.Kryukova, E.A.Paukshtis, V.V.Popovskii, T.G.Starostina, V.F.Anufrienko, V.A.Razdobarov, N.N.Bulgakov, A.V.Kalinkin. J.Catalysis, 1992, v.134, pp.506-524.
55. H.Knozinger, P.Ratnasamy. Catal. Rev. -Sci. Eng. 17(1978) 31.
56. J.Y.Yan, M.C.Kung, W.M.H.Sachtler, H.H.Kung., J.Catal. 1997, v. 172, N1, p. 178-186
57. Y.Teraoka, H.Ogawa, H.Furukawa, S.Kagawa. Catal. Lett., 1992, 12, 361
58. R.A.Grinsted, H.-W.Jen, C.N.Montreuil, M.J.Rokosz, M. Shelef. Zeolites, 1993, v. 13, No 8, p. 602 -606.
59. J.N.Armor, Th.S.Farris. Appl. Catal. B: Environ. 1994, v. 4, No 1, p. L11- L17.
60. P.Budi, R.F.Howe. Catal. Today 1997, v. 38, No 2, p. 175-180
61. A.Martin, H.Berndt, U.Lohse, U.Wolf. J. Chem. Soc. Farad. Trans. 1993, v. 89, No 8, pp. 1277-1282.
62. A.Yu.Stakheev, C.W.Lee, S.J.Park, P.J.Chong. Appl. Catal. B: Environ. 1996, v. 9, p. 65-76.
63. S.F.Tikhov, G.V.Chernykh, V.A.Sadykov, A.N.Salanov, G.M.Alikina, S.V.Tsybulya, V.F.Lysov. Catal. Today 53, 639-646 (1999).
64. A.Takami, T.Takemoto, H.Iwakuni, K.Yamada, M.Shigetsu, K.Komatsu. Catal. Today. 35, 75 (1997).
65. A.Takami, T.Takemoto, H.Iwakuni, F.Saito, K.Komatsu. SAE Trans. Section 4 No. 950 746, 521 (1995).

# ULTRASONIC INTENSIFICATION OF REAGENT AND ELECTROCOAGULATION TECHNIQUES OF WASTEWATER TREATMENT FOR REMOVAL OF HEAVY METALS, SURFACTANTS AND OIL PRODUCTS

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Nowadays, the preservation of the hydrosphere stands among the most pressing environmental issues, because of the increasing water consumption and contamination, caused by industrial and domestic wastes.

In Russia, current global use of river water already reached 13%. As a result, a lot of Russian regions face fresh water deficiency. Irretrievable water consumption in basins of the Kuban, Don, Ural, Terek and other rivers surpassed the environmentally safe level and human activities are responsible for the majority of the heavy damage to the hydrosphere.

Electrocoagulation- and reagent-based wastewater treatment technologies for removal of anthropogenic contaminants, such as greases, oily emulsions, and heavy metal salts are extensively used at water treatment facilities of mines, metallurgic and food industries, and at municipal depuration plants.

Effluents carrying heavy metals are an undesired side-effect of some technological processes of industrial production, for instance electroplating and galvanoplastic coating, chemical and processing industries, maintenance of motor vehicles, car washers, etc. Heavy metals, e.g. lead, mercury, zinc, copper, cadmium, received by watercourses accumulate, through food chains, in bodies of animals and fish that die from intoxication or poison people who eat them. There are known cases of human intoxication with mercury, due to the consumption of fish.

An acute problem for urban areas is the removal of detergents (synthetic cleaning agents) getting into the sewage systems from laundries and “wet” cleaning services.

Year after year, the growing use of oil and its derivatives in industrial and transportation sectors increases severity of the problem of oil-contaminated wastewater treatment. The oil film brings imbalance to the gas and moisture exchange between the atmosphere and hydrosphere, resulting in a slowdown of the photosynthesis and oxygen release by phytoplankton, death of fecundated spawn, and other severe environmental effects.

The needs for better water treatment quality and reduction of the treatment time demand more intensive use of reagents and electrocoagulation techniques. Higher efficiency of such methods may be achieved through the application of ultrasounds.

Sonication (ultrasonic treatment) dramatically improves wastewater depuration, this technique may lead to savings in operational and capital costs when introduced both at existing or newly projected water treatment plants.

Various aspects of the ultrasonic effect on the treatment process by electrocoagulation of simulated and actual effluents containing non-ionic surfactants (NS) have been examined on a laboratory-scale pilot plant.

The ultrasonic effect was studied with respect to the changing of anode current and voltage parameters, to the foam formation and suppression, to the hydroxide residue formation and compaction, and to the temperature and pH variations in the examined solutions.

On-site experiments (with a large range of items) were performed at plants of the *Ayaks* company, which offers laundry and wet cleaning services. The results revealed a decline in concentrations of NS, suspended particles and other contaminants when electrocoagulation was implemented adding an ultrasonic treatment.

For instance, a 5 min. run of ultrasound-assisted treatment resulted in an NS concentration decrease of 5 - 30% and a 7.5 min. run - 0 - 15 % against the control samples, depending on the NS starting concentration and applied current value.

The largest difference in the transparency value between the test samples and respective controls was detected after the treatment with a 7.5 min. run (40 cm vs. 12.5 cm). For turbidity the maximum decrease was achieved after a 5 min. run (55 mg/l vs. 195 mg/l).

The colour of the tested sample treated for 5 min. or longer did not differ from colour of distilled water, whereas chromaticity of the dilute check sample was 3:1 after the 5 min. treatment and 2:1 after the 7.5 min. treatment.

Sonication impact on the efficiency of NS removal by electrocoagulation has been investigated using various anode current densities (0.03 - 0.1 A/cm2). Optimal parameters for current load and treatment time were identified using actual effluents.

The increment of the removal efficiency was 6 - 10% for the samples treated using ultrasound for 5 min. with a current load of 0.1 A/cm$^2$ for the tests performed after 1 and 3 days from the moment of sampling. Such value ranged from 76 to 85% and from 85 to 91% for the tests executed on samples after 5 days from the moment of collection. A drop of the current load to 0.03 A/cm$^2$ resulted in a 16 - 30% ultrasonic treatment quality rise (from 63 to 93% for the 5 min. treatment of the wastewater with a NS concentration equal to 1400 mg/l and from 69 to 85% for the 5 min. treatment of wastewater with a NS concentration of 550 mg/l). Thus the optimal anode current density was 0.03 A/cm$^2$; the maximum efficiency of the treatment with a starting NS concentration of 1400 mg/l occurred after the 7.5 min. treatment and scored 96% (vs. 82% of control). With a starting concentration of 550 mg/l, the maximum efficiency was 88% (vs. 79% of control).

Additionally, the effect of the addition of ultrasounds to electrocoagulation treatments of wastewater (for heavy metals removal) was investigated.

For all considered metals, cadmium, zinc, copper, and chromium (VI), the use of ultrasounds leads to a noticeable acceleration of the treatment process, if compared to the control treatments (without sonication). For the solutions containing just one metal, the efficiency of the treatment increased of 50 - 100%, depending on the current density. When few heavy metals were present in the solution, such increase was 30%.

The most appreciable ultrasonic effect was observed for heavy metals incorporated in anions (chromium (VI)), where, similarly to electrocoagulation removal of dyes, the ultrasonic efficacy grew with increasing density of current passing through the cell.

For cadmium, due to its low MPC (1 mkg/l) and relatively low electrocoagulation rate (even applying ultrasounds), it is necessary to use a two-step successive electrocoagulation process, including a flotation treatment with a coagulant-flocculant agent (e.g. AKFK).

Basing on the results of the laboratory tests, we designed and selected the key parameters of operational conditions for heavy metals removal from wastewater. However, additional researches, using existing pilot plants, are needed to study how ultrasound affects the processes of electrocoagulation-based removal of heavy metals.

In studying the regularities of the sonication on oily wastewater reclamation it has been established that:

1. In all operational schemes, a noticeable acceleration of water treatment occurred when using sonication, which allowed a 3 to 4-fold speeding up of the treatment runs.
2. As experimentally shown, the most effective protocol is the one based on a joint use of a flocculant-coagulant, like AKFK, and ultrasounds. Its efficiency is 1.5-2 times higher than that of a process with the Aurat type coagulant.
3. The use of a AKFK pre-treated with sonication in the electrocoagulation process makes it significantly more effective than the one using a non-treated coagulant.
4. Ultrasonic water treatment in the flotation cell should be conducted at intensities close to the cavitation threshold, i.e. at frequency 10 - 24 kHz.
5. To provide effective ultrasonic treatment in all the volume of the floater it is advisable to employ a combined technology using both radiating systems with a developed surface, e.g. a magnetostrictive waveguide (MTS), and hydrodynamic emitters. Best efficiency of ultrasounds is achieved in flotation cells with a diameter of 2.5 m and with at least 4 MTS-like emitters.
6. The experiments show that it is necessary to use simultaneously two types of sonication: a) the first is the pre-treatment of the AKFK solution under developed cavitation conditions in flow tanks, prior to addition to wastewater; b) the second is for the total volume of liquid, directly conducted in the flotation cell, at intensities that almost correspond to the cavitation threshold.
7. For water post-purification from phenols and sulphides it is possible to apply radiation by ultraviolet xenon tubes operating in the pulse mode; water treatment time is 5 - 10 sec.
8. The background data allow assuming that the alternative treatment scheme, which includes ozonation of the total treated wastewater volume, is less effective than ultraviolet radiation in the pulse mode.

Thus, the performed tests demonstrated technical feasibility and benefits of ultrasonic techniques in wastewater treatment for removing pollutants, such as NS, heavy metals and oil products.

# STRUCTURAL ORGANIZATION AND PHYSICO-CHEMICAL PROPERTIES OF NATURAL LIGNIN

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Lignin (from Latin *lignum* - wood, timber) is the second most abundant organic matter on Earth after cellulose. Lignin was discovered for the first time in plants of the Filices family. Its origin is related to on-land escalation of plants and a need in mechanic strengthening of stems and trunks. Back in 1832, Freidenberg [1, 2] suggested a theory about the role of lignin as a filler of plant cell walls. In this respect, lignin may be compared to cement in reinforced concrete. Recent researches have revealed a larger diversity of lignin functions in the vegetal organisms.

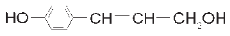
At present, it has become apparent that the term “lignin” is hardly applicable to a single chemical compound. It most likely defines a group of structure-related polymeric macromolecules. A common feature of lignin substances is their insolubility in wood treatment with concentrated sulphuric (72%) or hydrochloric (41%) acid. It is proved that lignin from different plants is composed of oxygen-containing phenylpropane intermediates characterized by a different methoxylation degree of aromatic nuclei.

Lignin is a chemical and morphological component characteristic of tissues of higher plants, such as pteridophytes and spermatophytes (gymnosperms and angiosperms). Its presence is typical for tissues with liquid-conducting (e.g. for xylem) and rigidity-enhancing functions. In lower plants (e.g. algae, fungi), its concentration is actually negligible.

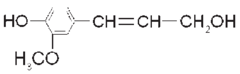
The lignin amount in wood shows rather broad variations, e.g. it makes up 25 - 30% in softwood and 9 - 23% in hardwood. Its concentration is governed not only by the plant species, but also by many other factors, such as climate, soil characteristics, age of the tree, etc. Moreover, its content varies across the tree structure. A major lignin fraction is found at the trunk bottom, at the top and in internal parts, in the conifer branches, in bark and in compressed wood. Examination of the wood structural arrangement at a cellular level has shown that lignin largely concentrates in the middle lamella and in the cell wall (about 25%). In addition, lignins located in these two parts of the plant tissue greatly differ in chemical and polymeric features.

In industry, lignin most often is not removed from wood. Only in wood chemical treatment technologies related to paper and pulp manufacture lignin is extracted in a modified or degraded form (delignification). The extracted lignin is a significant potential carbon source for chemistry and energy applications.

**Lignification of wood cell walls.** Lignin macromolecule formation in plant (lignification) consists of a system of complex biological, biochemical and chemical processes. Numerous researches proved that precursors of all lignins, i.e. original structural chains, are n-hydroxy cinnamyl alcohols: n-coumaryl (I), coniferyl (II) and sinapyl (III):



I



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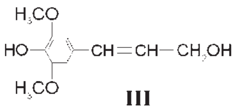

III

The lignin biosynthesis (Fig. 1) begins with the glucose generation during the photosynthesis. Glucose transforms to shikimic acid - an important intermediate of the so-called ‘shikimic acid’ pathway. Final products of this pathway are two aromatic amino acids, L-phenyl alanine and L-tyrosine, produced by reductive amination via prephenic acid. In their turn, the amino acids, serve as starting substances (the ‘amino acid totality’) for the enzymatic synthesis of phenyl-propanoid compounds (a ‘cinnamic acid’ pathway). This synthesis proceeds through activated intermediates of cinnamic acid to give off three cinnamyl alcohols as well as some extractive ingredients, such as flavonoids and stilbenes. Generation of lignin polymeric molecules from monomer precursors (monolignols) includes a stage of enzymatic dehydropolymerization of resonance-stabilized n-hydroxy cinnamic radicals and their random combinations (‘end-wise’ polymerization) yielding dilignols (dimeric structures), oligolignols and ultimately polylignol (lignin), a branched polymer. During polymerization, in addition to linkage of radicals, ionic reactions occur with the participation of intermediate quinone methides. In this context, it is possible to conclude that lignin macromolecules are formed by random linkage of lignols yielding a non-linear polymer rather than by a genetically predetermined regular process. Hence, the final structure of the polymeric product is governed primarily by reactivity and frequency of participation of structural polymerization chains. A diversity of bonds emerging among individual structural elements during lignin formation leads to a polymer with irregular structure, a so-called ‘lignin macromolecule’.

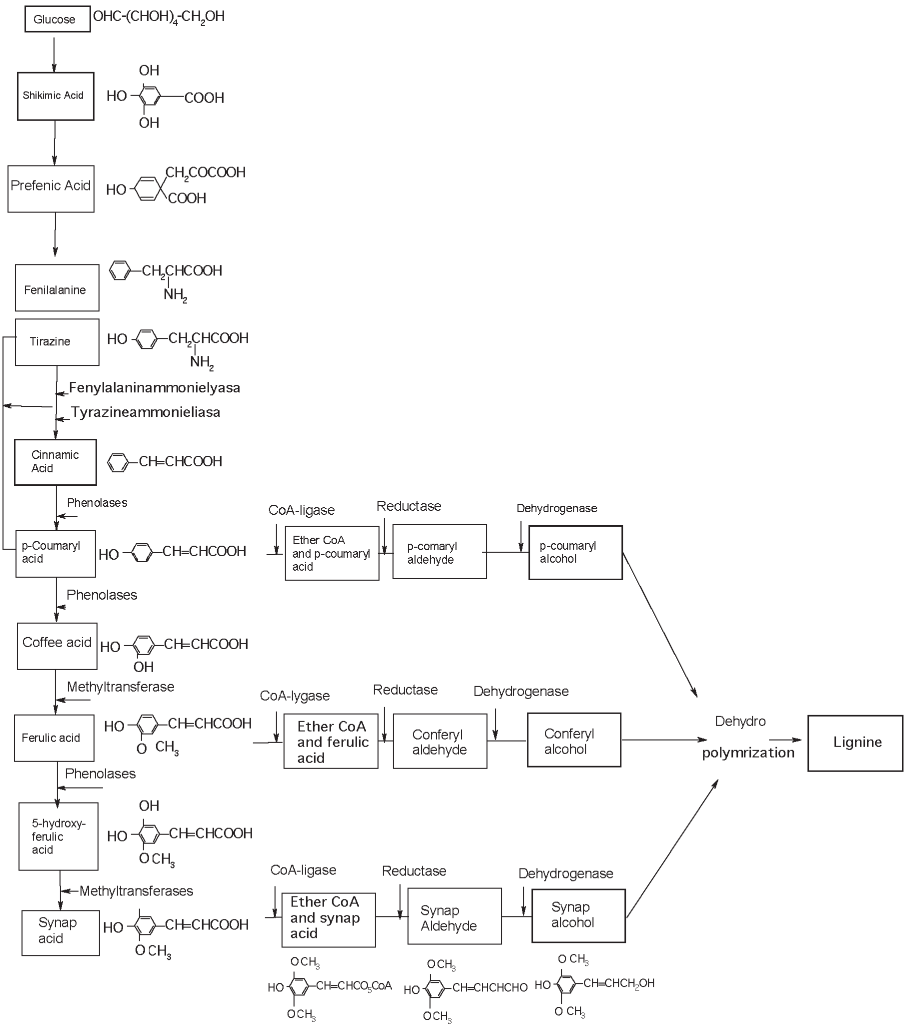

**Fig.1. Biogenetic relation of phenolic compounds in plants [2].**

A distinctive characteristic of lignin as a polymer is its singular nature deriving by the different features of the micro-structural elements, which make up its macromolecule. Heterogeneity and chaos - typical for different levels of the lignin polymer structure - are genetically predetermined by the structure of the monomeric phenoxyl radicals, capable of existing in various mesomeric forms. At the same time, lignin is characterized by a certain internal ordered arrangement despite its irregular chemical structure and chaotic cross-linking chains. This is evidenced by the implementation of the fundamental principle of the ‘scaling invariance’, a general feature for polymeric systems. The above is conditioned by dynamic self-organization processes, which occur during the lignin biosynthesis and lead to chaotic branching of the fractal structure in coniferous lignins and star-like topology in deciduous lignins [3, 4].

A lignin macromolecule fragment scheme proposed by Freidenberg (Fig. 2) deserves special attention. It is one of the more complete existing schemes, including modern understandings about the lignin structure and its basic properties and reactions. It was conceived considering the contemporary data on the quantitative composition of the various arrangements and structures in lignin. It also comprises experimental data from model substances and milled lignin, as well as results of researches in lignin biosynthesis. This scheme is not a lignin structural formula and it cannot be regarded as definitive. It is impossible to exactly reproduce all lignin structural elements and bonding types. Nevertheless, this scheme takes into account the most important available data on the lignin structure and is consistent with the basic properties of natural lignin.

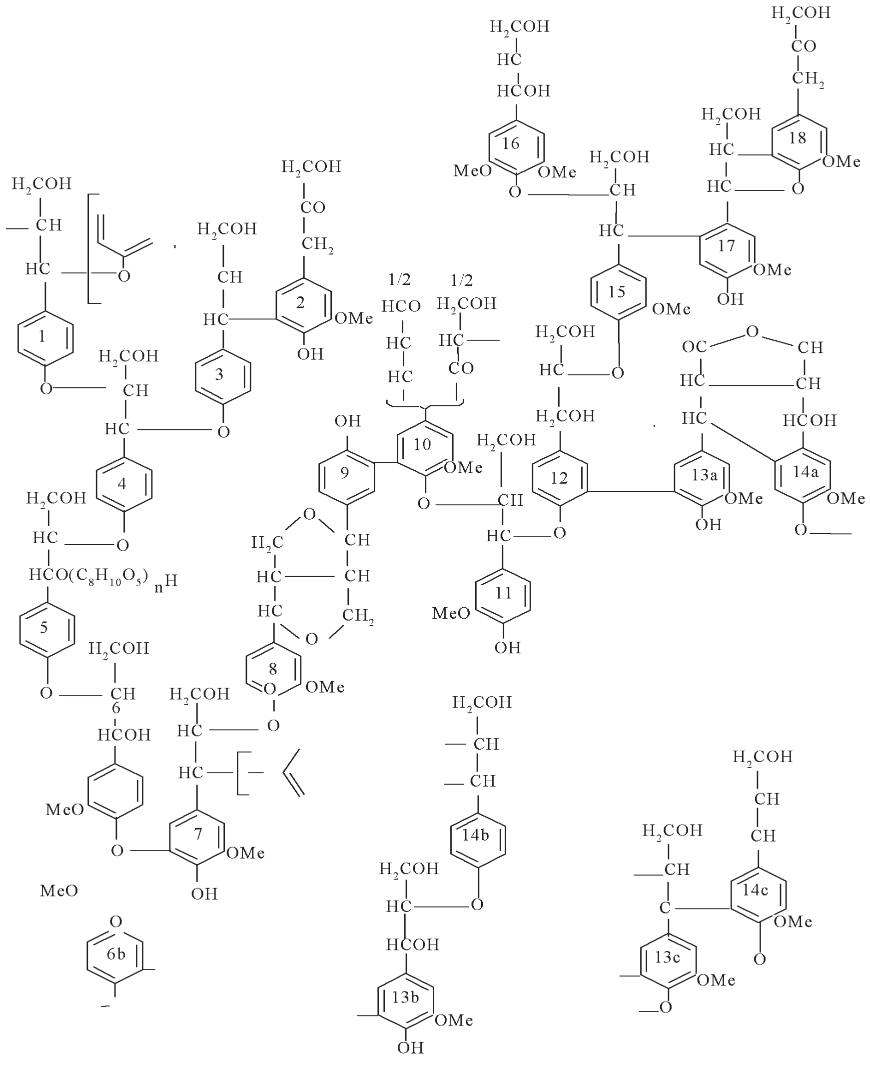

Fig.2a. Scheme of lignin macromolecule fragments in softwood [1].

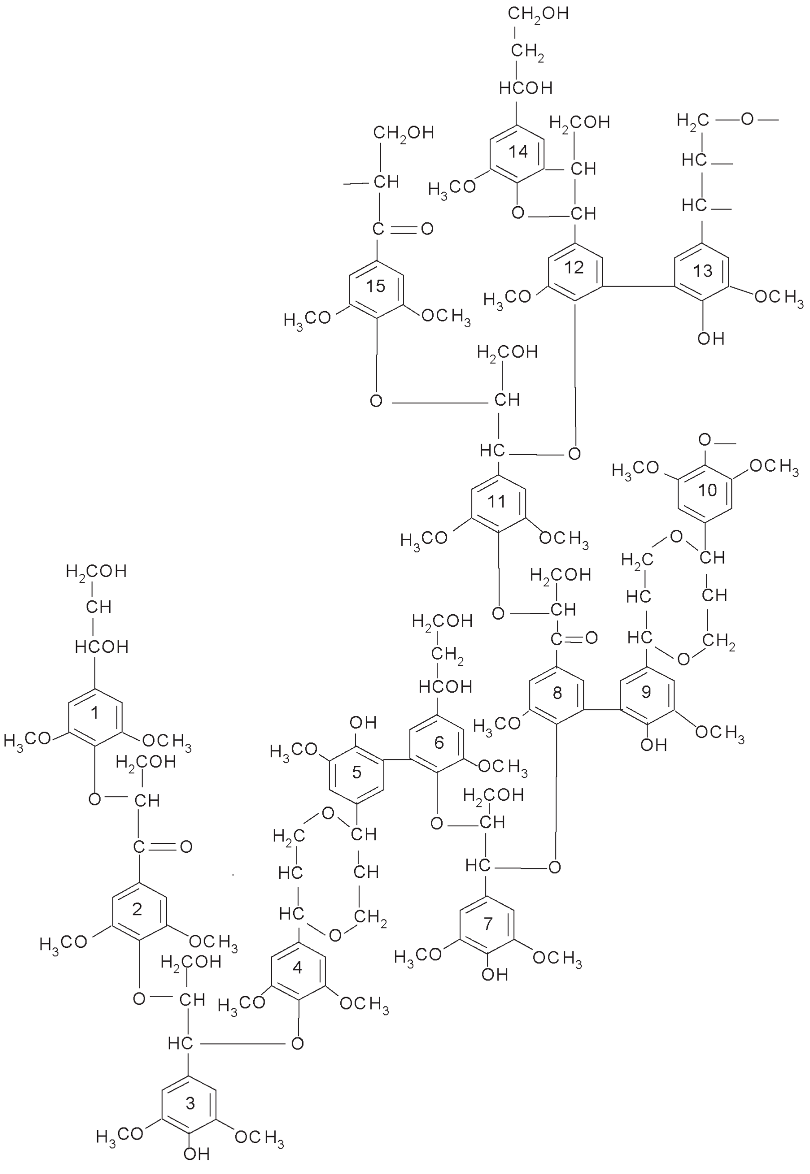

**Fig.2b. Scheme of lignin macromolecule fragments in hardwood [1].**

**Acid-base and redox properties of lignin.** The acid ionization ability of lignin fragments has a determining effect on the lignin biosynthesis and its reactivity in the course of wood delignification. Due to that, the recent years have been marked by a reviving interest about the studies on acidity of phenolic structures and exposure to external factors, such as temperature, solvent nature, ultraviolet irradiation, etc.

Different authors and research teams both in Russia and worldwide carried out extensive investigations about acid-base properties of lignin structural units in aqueous solvents, basing on examples of low-molecular phenols with a similar structure [5-11]. Depending on the properties of substituents in the aromatic ring, $pK_a$ values of such compounds vary within the range of 7.4 - 10.5 units, provided Hammet equation is strictly observed.

Phenol hydroxyl groups, like phenolate anions, are known to be capable of specific solvation by solvent molecules owing to rather strong hydrogen bonds detected by UV and IR spectra. Because of that, solvent composition modification is a mighty tool to control acidity of phenolic compounds. This is clearly visible in mixtures of water with dipolar aprotonic solvents extensively applied in wood chemistry. Currently available methods allow determination of thermodynamic constants of phenol acid ionization in non-aqueous media and their collation, using infinitely diluted solution as reference and acidity scales based on evaluation of the parameter $pa_{H+}$ [12]. It was shown in [13] that switching solvent from water to DMF or DMSO, acidity of lignin model-compounds lowered by 5 - 7 orders, where the $pK_a$ value linearly depends on the molar fraction of the organic co-solvent. Additional data on phenol solubility made it possible to split such overall solvation effect into separate constituents for the phenol neutral form and for the relevant anion. That helped ascertain that the determinant factor of the aprotonic solvent effect on lignin fragment acidity is energy destabilization of the phenolate anion, during its transfer to the medium with minor electron-donating capacity.

Due to the diversity of structural fragments considerably differing in acidity, the lignin macromolecule generally cannot have a definite true $pK_a$ value. To this end, in order to characterize the acid-base properties of lignin as a polymer, the qualitative difference between lignin and low-molecular phenols must be considered. This refers to the existing hydrogen bond network among independent macromolecule fragments, including those with participation of acid groups, as well as to related conformational fragments, which are able to affect the accessibility of polymer reaction sites. In addition data from the studies on the macromolecule functional composition and prediction of acidity of relevant structural units - based on the data on model compounds in a particular solvent - must be considered. In [14, 15], the authors assume that a certain microzone inaccessible for solvents and various reagents is likely to exist within the lignin macromolecule. Ionization of acid groups located in the molecule hydrophobic nucleus proceeds with higher pH values than at titration when such group is completely exposed to alkali, due to a dielectric permittivity decline in this internal zone. The profound effect of hydrogen bonds on lignin acidity is proved by the experimental drastic change of $pK_a$ when small quantities of reagents facilitating the H-net breakage (normally used for protein denaturation, e.g. urea, methylcellulose) are added to the system [16]. Another important factor affecting acidity of the macromolecule is its polyelectrolytic properties. If a polyion is charged negatively, its electrostatic field prevents basic ions from penetrating deeply inside of the macromolecule. As a result, experimental $pK_a$ values appear to be overstated. The error in evaluation of the acidity constant fast increases along with the molecular mass, reaching 3 units for high-molecular samples. This effect is accompanied by a major scattering of the titration curve.

Schtrace [17] proposed a method for evaluating average $pK_a$ of lignins by their spectrophotometric titration relative to neutral solution. The pH value of the titration curve corresponding to 50% ionization degree of phenol hydroxyl groups is accepted as an average or ‘mixed’ $pK_a$. Average $pK_a$ values of lignins defined by this method in [18] appeared to be rather high and comprised 11.0 for alkaline lignin and 10.9 for alkaline sulphate lignin. Basically, optical density measurements for a few wavelengths allow a somewhat credible estimation of average ionization constants at least for two phenol hydroxyl groups considerably varying in acidity. This approach was employed by the authors [19] to characterize acidity of Bjorkman lignin fractions. The results obtained demonstrate an effect that seems surprising at first sight: $pK_a$ lowers noticeably with the molecular mass growth, i.e. acidity of larger macromolecules approaches acidity of monomeric phenols.

It is possible to explain this fact assuming that the influence of hydrogen bonds might also have a direction opposite to that of the electrostatic factor. In the studied samples, it may imply preferable participation of the primary (ionic) form of acid groups in the hydrogen bond, impeding proton addition and – correspondingly– involving a $pK_a$ decline.

According to Cassidy and Kun’s definition [20], lignins may be assigned to the class of redox polymers containing functional groups capable of reversible redox interactions (a phenol-quinone redox system). Chemical [21] and physico-chemical methods prevail in identifying the redox state of lignin structures, a very interesting one is indirect redoxometry. It bases on the examination of reactions of the studied lignin preparations with reversible redox systems (ROS), e.g. potassium hexacyanoferrate (II, III) [22-27].

A main physico-chemical parameter of the lignin redox state – the so-called ‘effective potential’ – is a function of the organic substrate structure and a factor affecting its behaviour in redox reactions [28]. This judgment stems from the studies on reactivity of model compounds of the lignin structural fragment. The effective potential values determined for dioxane lignin and Bjorkman lignin [29] prove the influence of factors like the wood nature, sample preparation technique, and macromolecular properties.

Effective potential ($E_0^*$) for lignin preparations was estimated by the equation used for calculating $E_0^*$ of model compounds [28]. It is based on the data on the pseudo-equilibrium between ROS, studied substrate (ArOH) and initial products of its oxidation represented by aroxonium cations ($ArO^+$):

$$E_0^* = E_0 + \frac{2.3 \times R \times T}{n \times F} \times \ln \frac{[Ox]_p^2 \times \gamma_{Ox}^2 \times [ArOH]}{[\mathrm{Re}d]_p^2 \times \gamma_{\mathrm{Re}d}^2 \times [ArO^+] \times [H^+]}$$

where:
$E_0$ - ROS standard potential, mV;
$[Ox]_p$ - concentration of the ROS oxidized form at equilibrium, mol/l;
$[Red]_p$ - concentration of the ROS reduced form at equilibrium, mol/l;
$\gamma$Ox, $\gamma$Red - activity factors of the ROS oxidized and reduced forms.

As the active site in lignin redox reactions is phenol hydroxide ionized by the solvent, there apparently exists a relation between the acid-base, redox, and macromolecular properties of this polymer [19, 29, 30]. In the close-to-native lignin preparations, not only the pK value, but also reactivity in redox reactions [19] decrease with the molecular mass build-up (i.e. the effective potential increases). When the molecular mass ($M_w$) is below 8,000, for dioxane lignin and Bjorkman lignin $E_0^* = 21.0 \times \ln [M_w + 662 \text{ (mV)}]$; at $M_w$ more than 8,000, for dioxane lignin $E_0^* = 21.3 \times \ln [M_w + 679 \text{ (mV)}]$ and for Bjorkman lignin $E_0^* = 32.6 \times \ln [M_w + 54]$. A portion of phenol hydroxyl groups participating in redox interactions also reduces proportionally to increasing molecular mass of the lignin preparation.

**Structure of natural lignin.** The issue of the natural lignin (protolignin) structure is of principal importance. On the one hand, it is associated with the understanding of the lignin location and role in the plant tissue structure. On the other hand, it determines a choice for the approach to estimation of the character of its transformations in technological processes. Anyhow, it is not easy to propose an unambiguous solution for this problem, because extraction of lignin bulk from the plant tissue – in the an unmodified form, using conventional chemical and physical methods for polymer investigations – is impossible due to its high lability.

At present, two protolignin structure and molecular mass theories exist, which could be conventionally tagged as the ‘three-dimensional network’ and the ‘solid solution’ [23].

*Three-dimensional network concept.* Freidenberg was the first to put forward an assumption on the protolignin three-dimensional structure and Goring developed its conceptual fundamentals. The theory bases on considering lignin as a cross-linked polymer that occurs in nature in the form of sol and gel fractions. The former is relatively low-molecular and soluble in organic solvents. That is Brauns 'native lignin', comprising about 10% of timber lignin. Lignin mostly consists of the gel fraction that forms an infinite three-dimensional network penetrating the entire plant tissue. Hence, the molecular mass of extracted lignins – ranging from $10^2$ to $10^5$ and even $10^6$ – merely characterizes the molecular mass of infinite three-dimensional network fragments. Thus, this concept regards the molecular mass of natural lignin as irrelevant.

*Solid solution concept.* Acceptance of this theory is currently increasing. It assumes woody substance to be a solid solution where basic wood constituents – i.e. cellulose, hemicelluloses and lignin - are linked by hydrogen bonds and the latter two components are connected by covalent bonds. Hydrogen bonding is the key linkage type of wood components. It develops an infinite network integrating the cellulose carcass and ligneous-carbohydrate matrix of cell walls. It also forms the plant tissue structure by means of intercellular substance. All the above is consistent with the approach to lignification and wood matrix structure formation in terms of physical chemistry of polymers [31]. It regards wood as a three-component system of natural polymers (lignin - hemicelluloses - cellulose). Its state is described by concrete values of thermodynamic parameters that characterize its stability level [32]. The correctness of this conclusion is confirmed by some facts: existence of a strong lignin-carbohydrate complex and availability of thermodynamic miscibility regions. This is true for the lignin-hemicellulose system with a lignin content in ratios 0÷11.2 % and 84.3÷100 %. It is also true for the hemicellulose-cellulose system at a component ratio 1:1. On the contrary these features are absolutely absent in the cellulose-lignin system [33, 34].

Different types of functional groups and structures, a mix of oxidized and reduced forms and chemical bonding capabilities are the factors that govern the thermodynamics of the redox polymer state in plants. Their impact is especially pronounced on molecular and supramolecular structural levels. In the course of the biogenesis both structural and functional transformation of the woody substance components occurs. At early stages of biological formation of a tree (early wood), lignin precursors are phenolic compounds with a small molecular mass. Their amount is relatively low if compared to carbohydrates. Yet they play an active physiological role in the plant organism, participating to cellular metabolism, redox reactions, and biosynthetic processes. A mechanism of phenolic compound formation in plants and the chemical nature of the components are likely to predetermine thermodynamic miscibility in the phenolic compound-carbohydrate system and to set rather strong lignin-hemicellulose chemical bonds. At the final stage of its formation, the lignocarbohydrate matrix consists of two rigidly combined interlacing networks of lignin and hemicelluloses (lignin solid solution in hemicelluloses). It is actually impossible to destroy such network fixed by hydrogen and chemical bonds and to separate hemicelluloses and lignin in a pure state [35].

With loss of biological plasticity during lignification, oxidative and dehydrogenation processes commence to drastically prevail over reduction. Polyphenol oxidation products deposit in the form of quinoids that catalyze biological processes. The resulting phenol-quinoid redox system of the lignin components leads to thermodynamic disequilibrium in the wood matrix, to lignin and cellulose thermodynamic non-miscibility, and - ultimately - to heterogeneity. Lignin domains that just start developing tend to a spherical shape. As the lignocarbohydrate matrix evolves, such domains become loose macromolecular formations with hemicellulose fragments (hemicellulose solid solution in lignin) embedded in lignin globules, which correspond to the region of their thermodynamic miscibility. Lignin domains are linked with the encircling carbohydrate matrix, owing to the available residual amounts of phenolic structures. Consequently, lignin in such solid solution differs from rigidly networked lignin in both functional nature and poly-molecular properties. It is more labile at wood exposure to external factors with respect to the carbohydrate matrix.

Elemental cellulose fibrils (fibres) are generated in the presence of hemicelluloses. Due to limited miscibility of these polysaccharides, lamination of the binary hemicelluloses-cellulose system occurs with cellulose molecules accumulating and growing. It is accompanied by generation of elemental fibrils surrounded by a hemicellulose gel. The cellulose molecule linear structure, hydroxyl groups, and cross-linking of cellulose macromolecules by hydrogen bonds contribute to fibril crystal structure formation. In parallel, a thermodynamically unstable transition layer develops on the fibril surface owing to the diffusion of hemicellulose molecules with related chemistry. The layer consists of hemicelluloses and cellulose in equal proportions. A stringent hemicellulose molecule orientation along cellulose fibrils is observed. In a few instants, the diffusion is so deep that hemicelluloses hamper close grouping of cellulose molecules and amorphous regions emerge in the cellulose structure. Diffusion processes in mixtures of polymers, close by nature though thermodynamically incompatible, are well explored. These processes often help improve mechanical characteristics of some polymer compositions to a level that seemed unachievable because of thermodynamic non-miscibility of the components.

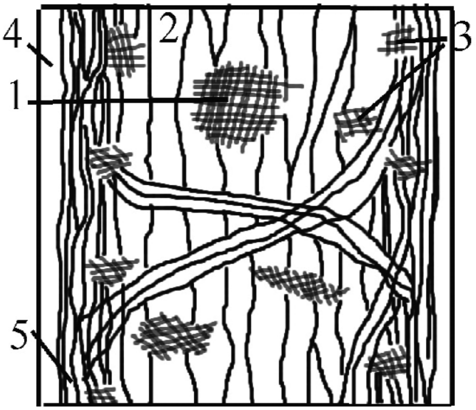

**Fig.3. Woody matrix model [35]: 1 - solid solution of hemicelluloses in lignin; 2 - hemicelluloses; 3 - solid solution of lignin in hemicelluloses; 4 - cellulose microfibrils; 5 - hemicelluloses-cellulose transition layer.**

Thus the lignocarbohydrate matrix is a superposition of interpenetrating networks (Fig. 3) produced by lignin hydrogen, carbon-carbon, and ether bonds and by lignin-carbohydrate bonds. Thermodynamically non-miscible cellulose and lignin create micro-heterogeneous regions surrounded by a hemicellulose gel. At the same time, hemicelluloses play the role of miscible agents by forming the transition layer on the surface of cellulose elemental fibrils and due to limited available thermodynamic miscibility with lignin. Compositions of lignin and hemicellulose macromolecule segments mechanically hitched both with each other and with cellulose add to the matrix strength.

The conclusion on thermodynamic non-miscibility in wood and a possibility of expanding non-miscibility regions of its components, owing to chemical and physical impacts, on the lignocarbohydrate matrix is of great importance. It defined a priority area in designing environmentally-safe alternative of woody material processing technologies to attain usable end products with preset properties for the consumers.

## CONCLUSION

Lignin ranks among the most abundant biopolymers. It is a complex mixture of macromolecules with a set of microstructural variables. Development of advanced environmentally-safe technologies demands in-depth exploration of lignin biosynthetic processes in plants and of its transformations in the course of woody material chemical processing. Additionally, it needs data on the structural arrangement of lignin macromolecules, lignin state in the cell wall of higher plants, influence of the macromolecular factors and environment on polymer reactivity, primarily, in acid-base and redox interactions. The discussed specific chemical and polymeric properties of natural and industrial lignin determine its special role in chemical processing of timber, first of all, for paper production. Industrial lignins, wastes generated in large amounts by the chemistry-forestry complex, are extensively utilized in construction, mechanical rubber production, mining, and other industrial and agricultural sectors.

Researches about new applications for lignin are far from being complete and will definitely continue. A key role belongs to the investigations focused on a deep study of lignin nature and properties.

## REFERENCES

1. Sarkanen K.V., Ludwig K.H. Lignins: Trans. from English, ed. by V.M. Nikitin. M.: Lesnaya Promyshlennost, 1975, 632p.
2. Fengel D., Vegener G. Wood (Chemistry, Ultrastructure, Reactions): Trans. from English, ed. by A.A. Leonovich. M.: Lesnaya Promyshlennost, 1988, 512p.
3. Karmanov A.P., Bogolitsyn K.G., Monakov Yu.B., Lunin V.V. Dehydropolymerization of monolignols and self-organized criticality. J.Phys.Chem. - 2003. - v.77. - no. 12. - p.2277-2282.
4. Karmanov A.P., Monakov Yu.B. Lignin. Structural Organization and fractal properties. Uspekhi Khimii. - 2003. - v.72. - no. 8. - p.797-819.
5. Mel'kis A.A., Zakis G.F. Meksha M.N. Acid-base titration of oxy- and ketocarboxylic acids and phenols related to lignin and its acidified intermediates. Wood Chemistry. - 1983. - no. 1. - pp. 106 - 112.
6. Chemist's Handbook. V. 3. - L.: Khimia, 1964. - 1005p.
7. Schtrace G.B., Nikitin V.M. Spectrophotometric technique for evaluating pK of alkali and alkali sulfate lignins and their model compounds. J.Appl.Chem. - 1967. - V. 40. - no. 8. - pp. 1814 - 1819.
8. Nordstrom C.G., Lindberg J.J. Thermodynamic ionization constants of phenolic acids related to cinnamic acid and lignin // Suomen. Kem. - 1965. - V. 38. - no. 12. - p. 3291-3295.
9. Ermakova M.I., Kiryushina M.F., Zarubin M.Ya. Comparison of OH-acidity of lignin-related phenols in water, alcohol and water-alcohol mixtures. Wood Chemistry. - 1984. - no. 5. - p. 23 - 29.
10. Gorbova N.S., Kosyakov D.S., Bogolitsyn K.G. The protolytic properties of lignin model compounds in mixed solvent DMSO - water / «Advances in lignocellulosics chemistry towards high quality processes and products»: Abstracts of Sixth European Workshop on Lignocellulosics and Pulp, France, 2000, 3 - 6 September, p. 339 - 342.
11. Bogolitsyn K.G., Lindberg I. Evaluation of OH-acidity of model compounds of the lignin structural fragment by a method of derivative UV spectroscopy. Wood Chemistry. - 1986. - no. 4. - p.56-60.
12. Gorbova N.S., Bogolitsyn K.G., Kosyakov D.S. Development of a potentiometry technique for estimation of ionization constants of model lignin compounds in DMSO and its aqueous mixtures. Univ. Bull. Forest Journal. - 2000. - no. 4. - p.111 - 116.
13. Bogolitsyn K.G., Gorbova N.S., Kosyakov D.S. Acid-base properties of phenols related to lignin in the water-aprotic solvent system. Russian Journal of Physical Chemistry. - v. 77. - 4 - 2003. - pp. 590-594.
14. Chuiko G.V., Chupka E.I., Obolenskaya A.V., Nikitin V.M. Research on the kinetics of alkali absorption by dioxane lignin. Wood Chemistry. - 1971. - no. 10. - p. 133 - 136.
15. Chupka E.I., Obolenskaya A.V., Nikitin V.M. Influence of the lignin structure on some of its properties. Wood Chemistry. - 1970. - no. 5. - p.53 - 58.
16. Chuiko G.V., Chupka E.I., Obolenskaya A.V., Nikitin V.M. On effect of physical factors on identification of acid groups in lignin. Wood Chemistry. - 1971. - no. 10. - pp.133 - 136.

17. Schtrace G.B., Nikitin V.M. Spetrophotometric method to determine pK of alkali and sulfate lignins and their model compounds. J.Appl.Chem. - 1967. - no. 8. - p.1814 - 1819.
18. Schtrace G.B. Examination of lignin acidic properties modification during alkali cooks. PhD Diss. - L. - 1968. - 162 p.
19. Samylova O.A., Aizenstadt A.M., Bogolitsyn K.G., Kosyakov D.S., Gorbova N.S. Acid-base properties of Bjorkman lignin. Univ. Bull. Forest Journal. - 2003. - no. 6 - (in press).
20. Cassidy H.G. and Kun K.A. Redox Polymers: Trans. from English/Ed. by V.A. Korpachev. - L. - 1967. - 270p.
21. Zakis G.F. Functional Analysis of Lignins and their Derivatives. - Riga: Zinatne, 1987. - 230p.
22. Bogolitsyn K.G., Krunchak V.G. Theory and Practice of Redoxometry in Wood Chemistry. Wood Chemistry - 1989. - no. 6. - p.3-21.
23. Bogolitsyn K.G., Reznikov V.M. Chemistry of Sulfate Wood Delignification Methods. M.: Ekologia, 1994, 288p.
24. Aizenstadt A.M., Bogolitsyn K.G., Poltoratsky G.M., Krunchak M.M. Thermodynamic characterization of the reversible redox system potassium ferri-ferrocyanide. J.Appl.Chem. - 1984. - no. 10. - p.2247-2249.
25. Bogolitsyn K.G., Aizenstadt A.M., Poltoratsky G.M., Krunchak V.G. Stability of iron II and III cyano complexes in water. J.Appl.Chem. - 1987. - no. 9. - p.1965-1969.
26. Bogolitsyn K.G., Aizenstadt A.M., Poltoratsky G.M., Khabarov Yu.G. Assessment of the reducer reduction degree in the potassium ferricyanide-ferrocyanide system. Univ. Bull. Forest Journal. - 1987. - no. 5. - p.2138-2141.
27. Bogolitsyn K.G., Aizenstadt A.M., Poltoratsky G.M., Krunchak V.G. Role of oxygen in self-reduction processes of iron (III) cyano complexes. J.Appl.Chem. - 1987. - no. 10. - p.2199-2203.
28. Aizenstadt A.M., Bogdanov M.V., Bogolitsyn K.G. Reactivity of model compounds of the lignin structural fragment. Univ. Bull. Forest Journal.- 1998. - no. 2. - p.83-89.
29. Aizenstadt A.M., Bogdanov M.V., Bogolitsyn K.G., Kosyakov D.S., Krivonogova O.E. Assessment of lignin preparations reactivity. Univ. Bull. Forest Journal. - 2000. - no. 5-6. - p.145-151.
30. Samylova O.A., Aizenstadt A.M., Bogolitsyn K.G., Bogdanov M.V., Chukhchin D.G., Morozova Yu.G. Effective potential of coniferous low-modified lignin preparations. Univ. Bull. Forest Journal. - 2002. - no. 6. - p.98-107.
31. Bogolitsyn K.G. Development of scientific grounds for environment-safe alternatives of complex chemical treatment technologies of woody materials. Univ. Bull. Forest Journal. - 1998. - no. 2-3. - pp. 40-52.
32. Skrebets T.E., Bogolitsyn K.G., Gur'ev A.Yu. Thermodynamic miscibility of wood components (review). Wood Chemistry. - 1992. - no. 4-5. - pp. 3-11.
33. Gur'ev A.Yu., Bogolitsyn K.G., Skrebets T.E. Study of thermodynamic miscibility of lignin-hemicellulose system by water vapor static sorption method. Wood Chemistry. - 1993. - no. 4. - p.3-5.
34. Gur'ev A.Yu., Bogolitsyn K.G., Skrebets T.E. Thermodynamic miscibility in lignin-cellulose and hemicellulose-cellulose systems. Wood Chemistry. - 1994. - no. 1. - pp. 3-5
35. Gur'ev A.Yu., Bogolitsyn K.G., Skrebets T.E. Wood cell wall as a natural polymer composition. Wood Chemistry. - 1994. - no. 1. - pp. 6-7.

# GREEN CHEMISTRY METHODS IN CELLULOSE PRODUCTION FROM BIRCH WOOD

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Wood biomass is a constantly renewable organic raw material for production of valuable chemicals. Cellulose pulping is the quantitatively prevalent operation among chemical processes of wood transformation. Currently, important research topics in this field relate to the development of new wood delignification technologies. The latter are useful for improving yield and quality of cellulose, along with environmental safety of its manufacture.

One of the key objectives is the cellulose feedstock expansion, possibly using low-value waste wood in the productive process. In Russia, birch falls within the low-cost wood pool, being one of the dominating forest species. Specific features of the chemical composition of birch wood, i.e. high density and abundance of hemicelluloses, constrain its use in traditional technologies of cellulose production.

At present days, new concepts for environmentally-safe cellulose production technologies are being studied. They are based on wood delignification by organic solvents (solvolysis delignification) and oxidative delignification by oxygen in caustic soda or soda media (oxygen-alkali and oxygen-soda delignification). The processes of wood delignification using "clean reagents", as molecular oxygen or hydrogen peroxide, are remarkable for a number of benefits. They feature absence of disturbing odours, coming from emissions of sulphur-containing gases, low toxicity of wastewaters, and improved whiteness of cellulose. Thus it possible to avoid a stage of cellulose bleaching using hazardous chlorine compounds.

Solvolysis delignification by water-organic or organic reagents, e.g. acetic and formic acids, alcohols, phenols, allows complete utilization of the other wood components [1-3]. Exhausted alkali solutions of the solvolytic treatment contain lignin and hemicelluloses destruction products represented by phenols, low-molecular acids, and neutral substances. Some of them return to the technological cycle as delignification agents, the other can be transformed into valuable chemicals.

Various catalysts and oxidants (e.g. hydrogen peroxide) have been proposed for intensifying the solvolytic delignification processes. Various conditions for aspen and silver-fur wood delignification using acetic acid with addition of $H_2O_2$ and $H_2SO_4$ as catalysts have been investigated [4-6]. It has been established that, for these wood species, the temperature of 120-130°C and duration for 2-3 hours are optimal conditions. They allow preparation of a cellulosic product with a satisfactory yield and high cellulose content. Delignification results can be improved if an optimal ratio between acetic acid and hydrogen peroxide is selected, thus promoting the generation of peracetic acid. The latter facilitates deep lignin oxidation and increases wood delignification [7].

Higher promoting effect of catalyst additives ($H_2SO_4$, $TiO_2$, $Na_2MoO_4$) in wood delignification was observed using more diluted aqueous solutions (20:1), minimizing diffusion constraints [8. 9].

A number of publications provide data on cellulose production from birch wood by delignification using a mixture of ethanol, sodium sulphide, and alkali [10], concentrated acetic acid and $H_2SO_4$ [11], as well as on delignification of birch wood blended with other tree species in a water-alcohol medium [12, 14].

Some methods for catalytic delignification using also organic solvents allow preparation of chemically pure cellulose characterized by a very low residual lignin value. In such cases it is possible to replace conditioned wood and cotton raw materials with cheaper wood waste for preparation of microcrystalline cellulose (MCC). MCC found wide application as biologically active dope, as filler and stabilizer for medicines, for concentration of microbial suspensions, and treatment and separation of cellulases. It is used as an additive to creams and gels for cosmetics and perfumes. In food industry it is exploited for manufacture of low-calorie dietetic foodstuffs, to give right consistency to ice-creams, creams, pastas, dressings and mayonnaises. MCC special applications include production of catalysts and adsorbents, aqueous latex emulsions and inks, and modification of polymeric coatings [15].

Available technologies for MCC production from wood are based on traditional methods of cellulose pulping, followed by its mechanical milling, acidic and alkaline hydrolysis treatment, filtering, rinsing, and drying. The existing technologies are multi-step and energy-consuming. Moreover, the use of reagents containing sulphur, chlorine and mineral salts make the productive process environmentally-unsafe.

The objective of this research was to examine the features of oxidative catalytic delignification of birch sawdust by an environmentally-friendly reagent like hydrogen peroxide in a diluted acetic acid medium. On these bases, we studied new methods for cellulose and MCC production which would possibly raise quality of the cellulose and improve environmental safety of its manufacture.

## EXPERIMENTAL

Birch sawdust from the trunk section (2-5 mm fraction) was utilized as starting raw material. The wood composition as % dry wt. was: cellulose, 41.3%; lignin, 19.9%; hemicelluloses, 30.3%, and extractive matter, 6.8%. The sawdust was pre-dried at 105°C until a constant weight was achieved.

For birch wood delignification, a mixture of acetic acid solutions in a 30% concentration and hydrogen peroxide in a 35% concentration at different $H_2O_2/CH_3COOH$ molar ratios was used. Sulphuric acid and a $TiO_2$ suspension were employed as catalysts. Delignification was carried out in a 200 $cm^3$ stainless steel reactor at a temperature range of 120 - 140°C, for durations of 1-3 hours with a water ratio varying from 7.5:1 to 15:1.

The solvolysis treatment of the fibrous product was conducted with an 'acetic acid-hydrogen peroxide' mixture without catalyst, similarly to a procedure commonly used by researchers to study the wood delignification process.

Cellulose and lignin concentrations in our fibrous product were analyzed using standard methods. The cellulose content in wood was measured by Kurschner methodology [16], total lignin in wood was determined using Komarov's modification of the sulphuric-acid method [16]. Finally, the average degree of polymerization (DP) of cellulose was investigated using GOST (State Standard) 9105-74, which measures viscosity of diluted copper-ammonia/cellulose solutions.

Data on the cellulose supermolecular structure were obtained by X-ray diffractometry (DRON-4) and IR spectrometry (Vector 22, Bruker).

## RESULTS AND DISCUSSION

### DELIGNIFICATION IN THE PRESENCE OF A SULPHURIC-ACID CATALYST

Our first goal was to select optimal conditions for birch wood oxidative delignification in an aqueous solution of acetic acid and hydrogen peroxide. To this purpose, we studied how the different factors like catalyst (sulphuric acid), temperature, time, and water content – along with ratios of acetic acid and hydrogen peroxide in the reaction mixture – influenced yield of the cellulosic product, as well as lignin and cellulose percentages.

**Influence of the sulphuric acid catalyst.** Previous studies indicated the optimal concentration of sulphuric acid as catalyst in silver-fur wood solvolytic delignification is approx. 2% wt. [6]. This $H_2SO4$ concentration was also employed in the study of the regularities of birch wood oxidative delignification in the acetic acid medium.

Data in Table 1 show that the sulphuric acid catalyst decreases the residual lignin amount in birch wood, during its delignification at 120°C and different $H_2O_2/CH_3COOH$ ratios. At the same time, $H_2SO_4$ reduces the cellulose output.

**Table 1. Influence of the sulphuric acid catalyst on the yield and composition of the cellulose product obtained by birch wood delignification using the 'acetic acid-hydrogen peroxide' mixture at temperature 120°C and a process duration of 2 h**

| **Yield and composition of the fibrous product*** | **Catalyst type** | | | |
|---|---|---|---|---|
| | **N/A** | | **$H_2SO_4$, 2 % of a.d.w.** mass** | |
| | **Molar ratio $H_2O_2/CH_3COOH$** | | | |
| | **0.3** | **0.5** | **0.3** | **0.5** |
| Yield, % of a.d.w. mass | 73.1/74.5 | 67.2/69.8 | 52.1/53.4 | 48.3/49.8 |
| Composition, % of a.d. cellulose product mass: | | | | |
| cellulose | 53.5/52.2 | 57.7/56.8 | 73.8/73.4 | 77.9/76.2 |
| lignin | 4.5/4.7 | 2.9/3.4 | 1.5/1.8 | 0.4/0.7 |

* numerator - water ratio 15:1, denominator - water ratio 10:1.
** a.d.w. - absolutely dry wood

As the $H_2O_2/CH_3COOH$ molar ratio grows from 0.3 to 0.5, the residual lignin concentration in the cellulose product drops from 1.8-1.5% down to 0.7-0.4%.

**Influence of delignification temperature.** Table 2 provides data on the influence of the birch wood delignification temperature and duration on the yield and content in cellulose and lignin.

At a delignification temperature of 120°C and water ratio 15:1, the yield of cellulosic product is 52.1% after 2 h. It contains 73.8% of cellulose and 1.5% of lignin. If temperature is raised to 140°C, the yield decreases to 47.8% with the same process duration. The maximum cellulose percentage in the solid product (88.2%) was detected after 3-hours delignification at 140°C. Residual lignin was actually lacking in this sample.

**Table 2. Influence of the birch wood delignification temperature on the cellulose product yield and composition ($H_2O_2/CH_3COOC$ ratio 0.3, $H_2SO_4$ content 2 % of a.d.w. mass**

| **Yield and composition of the fibrous product** | **Delignification conditions*** | | | | | |
|---|---|---|---|---|---|---|
| | **120°C** | | **130°C** | | **140°C** | |
| | **2 h** | **3 h** | **2 h** | **3 h** | **2 h** | **3 h** |
| Yield, % of a.d.w. mass | 52.1/53.4 | 49.2/49.7 | 51.5/52.3 | 46.2/47.3 | 47.8/48.6 | 46.8/46.9 |
| Composition, % of a.d. cellulose product mass: | | | | | | |
| cellulose | 73.8/73.4 | 80.2/78.4 | 77.5/77.4 | 81.3/80.9 | 83.9/82.9 | 88.2/81.7 |
| lignin | 1.5/1.8 | 0.7/1.4 | 1.1/1.3 | 0.4/0.9 | 0,1/0.7 | 0/1.9 |

* data are reported for two water contents, water ratio 15:1 / water ratio 10:1.

At a water ratio 10:1, maximum cellulose (83.9%) and minimum lignin (0.7%) in the fibrous product were identified after delignification at 140°C for 2 hours. However, a delignification time increase from 2 to 3 h leads to a lignin content growth to 1.9%. This may be due to the intensification of condensation processes at low "water concentration" and higher temperatures resulting in the generation of so-called "pseudolignin". A similar phenomenon was found during birch wood delignification in 90% and 80% acetic acid pulping solutions at a water ratio 5:1 [17].

Thus, using a mixture of acetic acid and hydrogen peroxide, the optimal temperature of birch wood delignification is 120-130°C. This ensures a satisfactory yield of the cellulose product with a lower lignin percentage.

**Influence of the water ratio.** The graphs in Fig. 1 show how the water ratio affects the cellulose product yield and composition during the birch wood delignification process at 120°C. Analogous features were observed during birch wood delignification at 130°C.

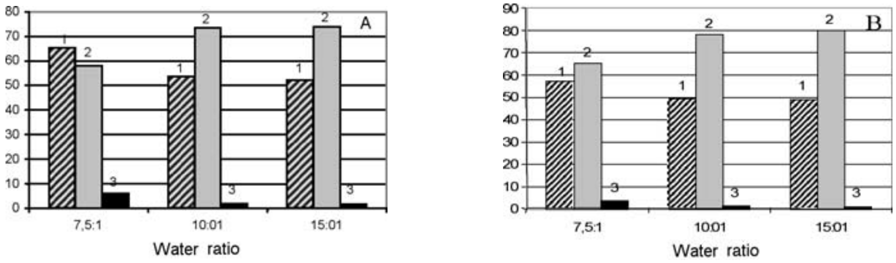

**Fig. 1. Influence of the water concentration on the yield and composition of the cellulose product obtained from birch wood at 120°C, $H_2O_2/CH_3COOH$ ratio 0.3, $H_2SO_4$ content 2% in weight and delignification time 2 h (A) and 3 h (B):**
**1 - product yield, 2 - cellulose content, 3 - lignin content**

According to our data, the water ratio is an important parameter of the process, which allows control of both the fibrous product yield and the cellulose and lignin amounts. At water ratios 10:1 and 15:1, the cellulose product is characterized by low residual lignin values.

A water ratio decreased to 7.5:1 raises both the cellulose product yield (55.4-62.7%) and residual lignin concentration (2.7-5.7%). A probable reason for that is hindered diffusion of lignin oxidation products from wood to solution, due to the deficient liquid phase. As a result, the "light" molecules produced by oxidative lignin fragmentation in the acidic medium are condensed to insoluble substances [18]. Additionally, lignin oxidation is slowed down by diffusion constraints of the oxidizing reagent transportation to the intercellular space of wood.

**Influence of the $H_2O_2/CH_3COOH$ ratio.** The residual lignin content in the cellulose product was minimal when a delignification solution with a $H_2O_2/CH_3COOH$ ratio equal to 0.5 was applied (Fig. 2). However, at a higher concentration of hydrogen peroxide, the cellulose product was yielded in dramatically lower amounts.

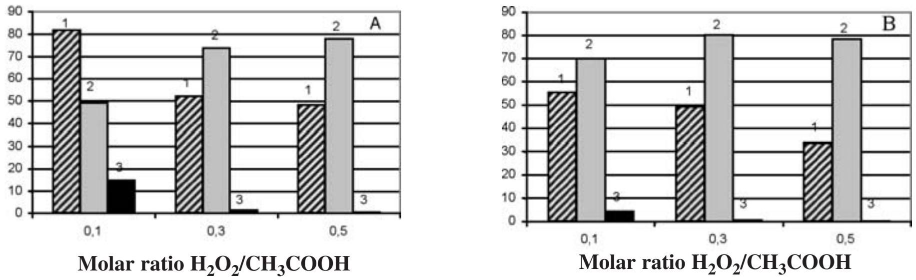

**Fig. 2. Influence of the $H_2O_2/CH_3COOH$ ratio on the yield and composition of the cellulose product obtained from birch wood at 120°C, water ratio 15:1, $H_2SO_4$ content 2% in weight and delignification time 2 h (A) and 3 h (B):**
**1 - product yield, 2 - cellulose content, 3 - lignin content**

Probably the increase of the $H_2O_2/CH_3COOH$ ratio initiated a growth of the concentration of hydroperoxide anions ($HOO^-$), which intensified oxidative destruction of lignin in the acidic medium [19] and simultaneously oxidized the amorphous fraction of cellulose.

A molar ratio $H_2O_2/CH_3COOH = 0.1$ for the reaction mixture was not appropriate to obtain a fibrous product with low lignin at temperatures 120°C and 130°C and delignification time of 2 hours. A prolongation of the delignification process to 3 hours decreased the residual lignin concentration to 4.3% - 3.2% and raised the cellulose content in the solid product up to 70.0% - 71.7%.

A $H_2O_2/CH_3COOH = 0.3$ or 0.5 ratio for delignification solutions allowed preparation of cellulose with chemical purity grade. Anyway, at the same time, we faced more efficient radical reactions leading to oxidative destruction of cellulose, resulting in a yield decrease.

## DELIGNIFICATION IN THE PRESENCE OF $TiO_2$

The $TiO_2$ catalyst suspended in the $H_2O_2/CH_3COOH$ mixture drastically decreased residual lignin in the course of birch wood delignification at temperatures 120-130°C. When $TiO_2$ was used as a catalyst, the delignification parameters, such as temperature, duration, $H_2O_2/CH_3COOH$, and water ratio affected the cellulose product yield and composition; patterns are generally similar to those evidenced for the use of sulphuric acid as catalyst.

Compared to $H_2SO_4$, the $TiO_2$ catalyst showed higher delignifying activity, thus allowing reduction of its concentration in the reaction mixture. Among the advantages of this catalyst are lacks of corrosion activity and environmental damage.

**Table 3. Data on the influence of the catalyst nature and birch wood delignification time on the cellulose product yield and composition (temperature 120°C, $H_2O_2/CH_3COOH$ ratio 0.3).**

| Parameters | $TiO_2$ (0.5 % wt.)* | | $H_2SO_4$ (2 % wt.)* | |
|---|---|---|---|---|
| | 2 h | 3 h | 2 h | 3 h |
| Yield of the cellulose product, % of a.d.w. mass | 79.9/81.3 | 50.5/62.8 | 52.1 | 49.2 |
| Composition, % of product mass: | | | | |
| cellulose | 50.8/49.4 | 79.2/66.9 | 73.8 | 80.2 |
| lignin | 8.8/9.2 | < 0.04/1.8 | 1.5 | 0.7 |
| Delignification degree | 64.7/62.4 | > 99.9/94.4 | 96.1 | 98.3 |

* data are reported for two water contents, water ratio 15:1 / water ratio 10:1.

The optimal $TiO_2$ content in the delignification mixture was 0.5% wt. Further additions did not lead to a decrease of the residual lignin in the cellulosic product. The parameters of the birch wood delignification process in the presence of catalysts $TiO_2$ and $H_2SO_4$ are compared in Table 3.

It is known [20] that destructive hydrolytic reactions of lignin in acidic media predominantly proceed via α-ether bonds of its structural fragments (Fig. 3).

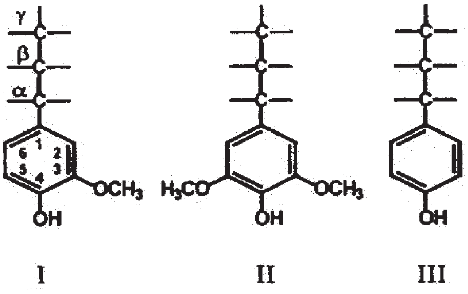

Fig. 3. Structural fragments of lignin

The hydrolysis of the α-alkyl ether bond in the acidic medium is carried out along the mechanism SN1. Simultaneously a reaction of α–β-elimination takes place leading to formation of enol ether. The rates of both reactions boost as the concentration of hydrogen cations increases. Elimination reactions are responsible of the accumulation of reactive double bonds in lignin. Along with their oxidation, lignin fragmentation occurs via β-ether bonds.

In aqueous solutions of hydrogen peroxide with organic and mineral acids, an electrophilic oxidizer is formed, i.e. a superacid:

$$H_2O_2 + RCOOH \longleftrightarrow RCOOOH + H_2O.$$

Hydrogen peroxide and superacid undergo degradation accompanied by the formation of free radicals when temperature rises and transition metal compounds are present. Note that the hydroxy radical $HO^{\cdot}$ is much more active than the peroxy one in lignin fragmentation reactions [21].

In acidic media, the formation of the hydroxy cation $HO^+$ is also possible. It initiates reactions of aromatic ring oxidative destruction, propane chain elimination, and opening of β-aryl ether bonds [20].

Hence, oxidative depolymerization of lignin in acidic media may follow both a radical and electrophilic mechanism. One or another mechanism prevails depending on the delignification conditions (temperature, $H_2O_2$ concentration and catalyst nature).

Interaction of lignin with hydrogen peroxide involves not only oxidation of the side chains, but also of the aromatic ring yielding different organic acids. Those acids can enhance the delignifying activity of the $CH_3COOH/H_2O_2$ mixture during cellulose production from wood.

On the base of the delignification activity data of catalysts $H_2SO_4$ and $TiO_2$, we can argue about the role of heterolytic and homolytic mechanisms of lignin oxidative destruction in the 'acetic acid-hydrogen peroxide' medium. Probably the heterolytic mechanism is prevalent when sulphuric acid is present, since this accelerates the hydrolytic decay of α-alkylaryl bonds. Differently the homolytic mechanism prevails in the presence of $TiO_2$, which is capable of initiating the formation of active hydroxyl $OH^{\cdot}$ radicals from hydrogen peroxide. Basing on the comparison of activity of the $H_2SO_4$ and $TiO_2$ catalysts during birch wood delignification (Table 3), we can assume that, in the $CH_3COOH/H_2O_2$ medium, homolytic oxidation is more effective than the heterolytic one.

## SOLVOLYSIS OF THE CELLULOSE PRODUCT

A method of catalytic oxidative destruction in the acetic medium was employed for developing a process of microcrystalline cellulose (MCC) preparation from birch sawdust. During industrial production, MCC is obtained via a hydrolytic treatment in the presence of mineral acids and various cellulose raw materials: sulphate and natron pulp, rayon cellulose and cotton fibres.

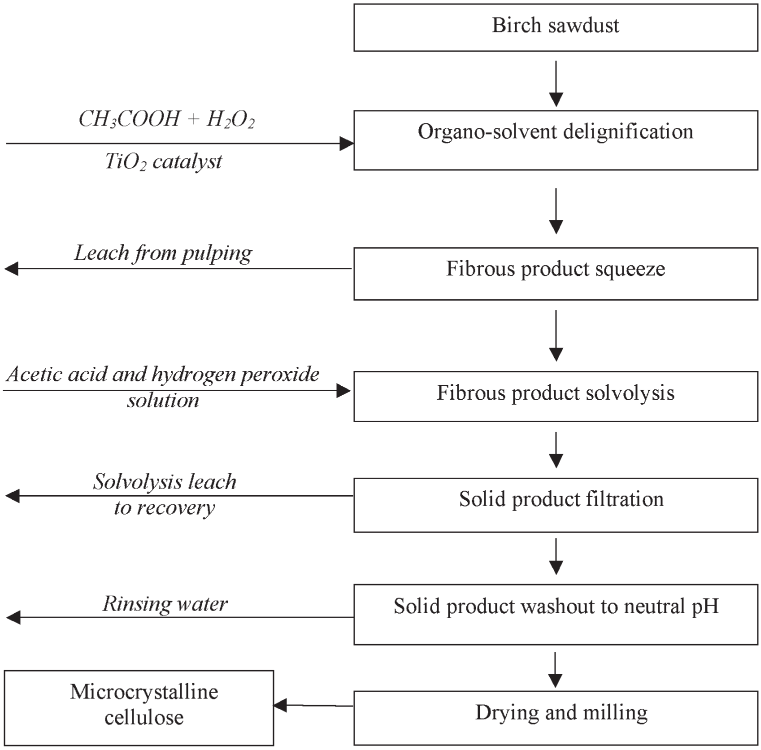

**Fig. 4. Scheme of MCC preparation from sawdust.**

The process we developed includes a step for cellulose preparation via birch sawdust oxidative delignification in acetic acid containing 0.5 % w/w of $TiO_2$ or 2% w/w of $H_2SO_4$. Following we applied a solvolysis step using a $CH_3COOH/H_2O_2$ mixture under optimized reaction conditions (Fig. 4).

**Table 4. Data on the MCC yield and degree of polymerization (DP) under various conditions of birch sawdust delignification and cellulose product solvolysis**

| Parameters | | | | | | MCC yield** | MCC DP |
|---|---|---|---|---|---|---|---|
| Delignification step | | | Solvolysis step | | | | |
| Temperature, °C | WR* | Time, hour | Temperature, °C | WR* | Time, hour | | |
| 120 | 15:1 | 2 | 120 | 10:1 | 1.5 | $\frac{73.1}{22.7}$ | 188 |
| 120 | 15:1 | 2.5 | 120 | 10:1 | 2.0 | $\frac{73.7}{31.6}$ | 94 |
| 120 | 15:1 | 3.0 | 120 | 10:1 | 1.5 | $\frac{67.4}{22.4}$ | 146 |
| 130 | 10:1 | 3.0 | 120 | 15:1 | 2.0 | $\frac{70.4}{24.1}$ | 150 |
| 130 | 12:1 | 2.0 | 120 | 15:1 | 2.0 | $\frac{58.7}{26.1}$ | 140 |
| 130 | 12:1 | 3.0 | 120 | 15:1 | 2.0 | $\frac{69.7}{19.7}$ | 177 |
| 130 | 12:1 | 2.0 | 130 | 15:1 | 2.0 | $\frac{64.4}{25.4}$ | 125 |
| 130 | 15:1 | 2.0 | 120 | 15:1 | 1.0 | $\frac{73.4}{26.6}$ | 226 |
| 130 | 15:1 | 2.0 | 120 | 15:1 | 2.0 | $\frac{68.4}{23.8}$ | 167 |

* water ratio

** higher percent value :MCC yield per fibrous product (dry wt.). Lower value: MCC yield per wood (dry wt.).

The cellulose amorphous fraction is dissolved during the solvolysis step, which allows obtaining cellulose of chemical purity grade, with a high crystallinity degree.

Table 4 demonstrates the influence of the conditions applied for the sawdust delignification and cellulose product solvolysis steps on the MCC yield and polymerization depth.

As follows from the diffractograms shown in Fig. 5, a crystalline cell of the birch wood-based MCC sample is identical to the crystalline monoclinic lattice of cellulose I. This conclusion was confirmed by the MCC spectra analysis.

The crystallinity index of the birch sawdust-based MCC sample is equal to 0.67. This value is close to crystallinity indices of MCC prepared from commercial sulphate (0.65) and sulphite (0.67) cellulose types and commercial MCC Avicel PH 102 (0.64).

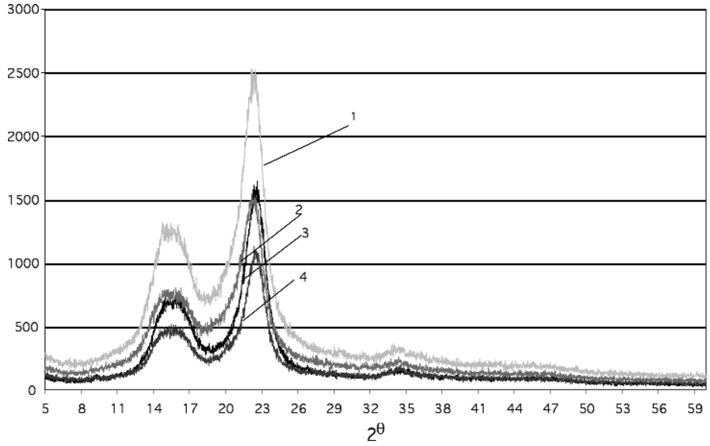

**Fig. 5. Diffractograms of MCC prepared from birch (1), larch (2), aspen (3) and silver fur (4) sawdust.**

## CONCLUSIONS

We obtained data about variation of yield and composition of the cellulosic product in different conditions – temperature, duration, reaction medium composition, catalyst nature – for catalytic delignification of birch sawdust using an ‘acetic acid/hydrogen peroxide’ medium.

It has been established that the optimal temperature of delignification lies in the range of 120-130°C where a rather high yield (up to 52.5% wt.) of the cellulosic product with a low residual lignin concentration (up to 1.1 % wt.) is achieved. At lower temperatures, residual lignin in the fibrous product dramatically increases, and a product yield decrease occurs at 140°C.

The catalysts $H_2SO_24$ and $TiO_2$ intensify birch wood delignification and thereby reduce both the lignin amount in the cellulose product and the process duration. The maximal yield of the product with the minimal lignin content was attained at $H_2SO_24$ and $TiO_2$ respective concentrations of 2% w/w and 0.5% w/w. Comparing their activities, we find that the route of homolytic lignin oxidation – in the presence of $TiO_2$ – is more effective than the heterolytic route of lignin oxidative elimination, initiated by $H_2SO_24$.

The increase of catalyst concentration leaded to a decline of the fibrous product yield, due to the intensification of radical processes of cellulose destruction. A similar effect was due to concentration of hydrogen peroxide. A value of 0.3 for $H_2O_2/CH_3COOH$ ratio was optimal, it ensured a rather high cellulose yield and residual lignin around 1.1%-1.5% wt. at 120-130°C.

A new organo-solvent alternative for cellulose production from waste wood (sawdust) was developed. It exceeds the traditional technologies in both efficiency and environmental safety.

This method was tailored for MCC production from birch sawdust. The proposed technology bases on the integration of two operational steps: birch wood catalytic delignification by an 'acetic acid/hydrogen peroxide' mixture at 120-130°C, followed by mild solvolysis of the product under analogous, but catalyst-free, conditions. Compared to existing traditional technologies for MCC production from wood, it shows some advantages: minimization of technological steps, higher quality of the final product, and lack of environmentally hazardous reagents, such as sulphur and chlorine congeners and mineral acids.

## REFERENCES

1. Pozdnyakov G.I., Ioffe I.I., Vishnevskaya CC. Solvolysis pulping - technology of the future. Bumazhnaya promyshlennost. 1987. no. 6. P.18-19.
2. Ioffe L.O., Ivanov Yu.S. et al. New technology of cellulose production offers environmental solutions. Bumazhnaya promyshlennost. 1990. no. 11. P.20-22.
3. Kuznetsov B.N., Efremov A.A., Kuznetsova S.A. Danilov V.G., Krotova I.V., Pervyshina G.G. Studies of organo-solvent pulping in the presence of various catalysts. Khimia rastitelnogo syrya. 1999. no. 2. P.85-90.
4. Danilov V.G., Kuznetsova S.A., Kudryashov A.V., Yatsenkova O.V. and Nikitina T.G. Aspen and silver-fir wood delignification in the presence of hydrogen peroxide and catalysts. Proc. Forth Int. Symp. "Catalytic and Thermochemical Conversions of Natural Organic Polymers".- Krasnoyarsk .- May 30-June 3 2000.- P.185-194.
5. Kuznetsova S.A., Danilov V.G., Kuznetsov B.N. Wood pulping in organic solvents in the presence of oxidizing reagents and catalysts. Proc. Sixth European Workshop on Lignocellulosics and Pulp. - September 3- September 6. -2000.- Bordeaux France .- P. 421-425.
6. Kuznetsova S.A., Danilov V.G., Kuznetsov B.N., Yatsenkova O.V., Alexandrova N.B., Shambasov V.K. and Pavlenko N.I. Environmentally Friendly Catalytic Production of Cellulose by Abies Wood Delignification in "Acetic A_id - Hydrogen Peroxide - Water" Media. Chemistry for Sustainable Development . 2003.-11.-P. 141-147
7. B.N. Kuznetsov, S.A. Kuznetsova, V.G. Danilov, I.A. Kozlov, V.E. Taraban'ko, N.M. Ivanchenko, N.B. Alexandrova. New catalytic processes for a sustainable chemistry of cellulose production from wood biomass. Catalysis Today, 75 (2002), PP. 211-217.
8. Kusnetsova S.A., Danilov B.G., Alexandrova N.B., Yatsenkova O.V., Kuznetsov B.N., Fat'yanova Yu.A.: Abies sawdust delignification by CH3COOH/H2O2 mixture in the presence of $TiO_2$ catalyst.- Proceedings of Seventh European Workshop on Lignocellulosics and Pulp "Towards molecular-level understanding of wood, pulp and paper" August 26-29, 2002 Turku/Abo, Finland, pp. 281-284.
9. Kuznetsov B.N., Danilov V.G., Kuznetsova S.A., Yatsenkova O.V., Ivanchenko N.M., Some regularities of wood delignification by CH3COOH/H2O2 in the presence of TiO2 and Molybdeniun catalysts, Book of Abstracts Russian-American Seminar "Advances in the Understanding and Application of Catalysts", Novosibirsk, 2003, P. 177-181.
10. Kordsachia O., Reipschlager B., Patt R. ASAM pulping of birch wood and chlorine free pulp bleaching. Pap. ja puu. 1990. 72. no. 1. pp. 44 50.
11. Sano Y., Maeda H., Sakashita Y. Pulping of wood at atmospheric pressure. I. Pulping of hardwoods with aqueous acetic acid containing a small amount of organic sulfonic acid. J. Jap. Wood Res. Soc. 1989. 35. no. 11. _. 991 - 995.
12. Karl W. Repap's Alcell process. Paper. 1991. V.215, no. 1. pp.46-47.
13. Acell can offer a Green solution. Pulp. and Pap. Int. 1991. V.33, no. 4. P. 53, 56, 57.
14. Harrison A. Repap produces high-quality pulp at Newcastle with Alcell process. Pulp and Pap. 1991. V.65. no. 2 pp. 116-119.
15. Petropavlovsky G.A., Kotelnikova N.E. Microcrystalline cellulose. Khimia drevesiny, no. 6, pp. 3-21
16. Obolenskaya A.V., Schegolev V.P., Akim A.G., Akim E.L., Kossovich N.L., Emelyanova I.Z. Practical Training in Wood and Cellulose Chemistry. M.: Ekologia.- 1991.- 319 C.

17. RF patent no. 2181807. A method of cellulose semi-product fabrication / Danilov V.G., Kuznetsov B.N., Kuznetsova S.A., Yatsenkova O.B. 27.04.2002, Bull. no. 12
18. NIKITIN B.M., OBOLENSKAYA A.V., SCHEGOLEV V.P. Wood and Cellulose Chemistry. M.: Lesnaya promyshlennost, 1978. -368 P.
19. DEMIN V.A., SHERSHOVETS V.V., MONAKOV YU.B. Reactivity of lignin and problems of its oxidative destruction by peroxy reagents. Advances in Chemistry, 1999.68. (11), P. 1029-1050.
20. FENGEL D., VEGENER G., WOOD (Chemistry, Ultra Structure, Reactions). Berlin.
    1. New York. Walter de Gruyter.1984.Fengel D., Vegener G. Wood. Chemistry, Ultra Structure, Reactions. M.: Lesnaya promyshlennost, 1988, 512 P.
    21. REZNIKOV B.M. Lignin transformations under hydrogen peroxide and molecular oxygen oxidation. Khimia drevesiny, 1991, no. 2, P. 3-11.

# HUMIC SUBSTANCES IN THE GREEN CHEMISTRY CONTEXT

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Among the environmentally-friendly substances with great potential in the field of green chemistry, natural compounds, namely humic substances (HS), deserve special attention. In the environment HS formation (humification) scores second after photosynthesis as process of organic matter transformation. It consumes about 20 Gt of carbon per year [1].

Interest into HS is currently increasing worldwide, production technologies are progressing and feedstock is expanding due to the involvement of new types of coal, peat, shale and peloids. Humic compounds are most extensively applied in crop production as an environmentally-safe alternative to fertilizers and, in some cases, pesticides.

Numerous researches have ascertained a stimulating effect of humic compounds on growth and development of plants, as well as on the increase of their insensitivity to adverse environmental impacts. A systematic use of humic agents improves the soil structure, its buffering and ion exchange properties, intensifies the activity of soil microorganisms and transformation of mineral elements into readily assimilated forms. Of special interest are the adaptogenic properties of humic substances that derive from their ability to bind radionuclides and heavy metal ions, destroy residues of pesticides, facilitate and speed-up detoxification of cultivated plants. Humic agents increase capacity of plants to withstand diseases, drought, excessive moisture, and cope with heavy doses of nitrogen salts in soil. They allow reduction of mineral fertilizer inputs without negatively affecting the crop, by improving assimilation of nutrients. HS also allow considerable limitation in application of pesticides, still preserving their efficiency; an extremely important feature for economy and environment.

Humic agents are usable not only for plant cultivation, but also for other sectors, such as cattle breeding, medicine, land reclamation, etc. However, marketable humic agents dramatically differ in properties depending on their source, production technology, and final form. For this reason the expansion of HS applications is currently constrained, as there is a gap in our knowledge, specifically a lack of investigations about quantitative description of the HS structure, properties, and action mechanisms. To this end, filling such gap is crucial for modern science.

## WHAT ARE HUMIC SUBSTANCES?

Humic substances (HS) are complex mixtures of dark-coloured organic compounds, with high-molecular weight and recalcitrant to biodegradation. They are generated during the decay of vegetable and animal remainders, caused by interaction of microorganisms and abiotic environmental factors [2]. HS constitute an organic macro-component of ground and water ecosystems as well as of solid fossil fuels. A generally accepted classification of HS [3, 4] bases on variations of their solubility in acids and alkalis. According to this scheme, HS can be classified as follows: *humin*, a non-extractable residue, neither soluble in alkalis nor in acids; *humic acids* (HA), a fraction which is soluble in alkalis and insoluble in acids (at $pH<2$); fulvo acids (FA), soluble both in alkalis and acids. The term “humus acids” is used as a generic name for both humic and fulvo acids. Humus acids are the most mobile and reactive components of HS, very active in chemical processes of ecosystems [1, 3, 4].

HS studies have a 200-year history. German chemist Ahard was the first to separate these substances from peat and describe them back in 1786 [5]. The first schemes of the HS isolation and classification were further developed by some German scientists [3]. They also introduced the term itself – humic substances (Huminstoffe) – that originates from Latin "*humus*" (ground or soil). A noteworthy contribution to the investigation of HS chemical properties was made by Swedish chemist J. Bercelius and his disciples in the middle of 19th century.

In the last century, significant advances in the HS studies were achieved thanks to Russian and Soviet researchers. Some of them became worldwide known, like M.A. Kononova, L.A. Khristeva, L.N. Aleksandrova, T.A. Kukharenko, D.S. Orlov, and others. However, in contrast to the European practice, HS investigations in soviet countries were among the areas of interest of geology and chemistry of the fossil fuels. Among the few exceptions there are some researches by the group of G.M. Varshal - a recognized specialist in the FA and migration forms of metals in water - who defended her D.Sc. thesis about this topic in 1994 [6]. For objectiveness sake, we should highlight that chemists in other countries showed less interest in this subject until that time. This mainly because in the beginning of the 20th century it was established that HS have a stochastic nature. Afterwards, their structural complexity was well illustrated by a model of a structural fragment of humus acids in soils, proposed by Kleinhempel in 1970 (Fig. 1).

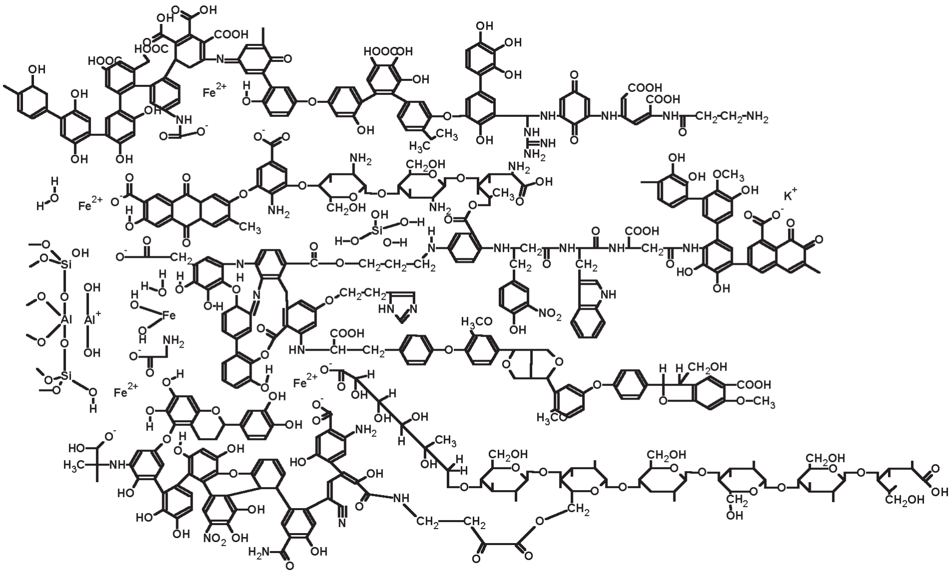

**Fig. 1. Hypothetic structural fragment of humus acids in soils [7].**

HS stochastic character originates from the specifics of their formation, which, in contrast to the biochemical syntheses of living matter, has no genetic code. The HS synthesis proceeds according to the principle of natural selection of structures most stable to biodegradation. The duration of their life cycles in the environment are estimated in the range of hundreds and thousands of years [2, 4]. The fundamental properties of humic substances include: non-stoichiometric composition, irregular structure, heterogeneity of structural elements and polydispersity. Thus, for them, the notion of *molecule* transforms into *molecular ensemble*, where each parameter is described by distribution. Therefore a traditional numerical description of the structure of organic compounds that characterizes the number of atoms in the molecule and number and types of their bonds, is also inapplicable to them.

The above model of an HS structural fragment explicitly shows why chemists are reluctant to get plunged into this “molecular chaos”. However, a deeper gaze at the HS composition and structure has established that the observable chaos is only apparent. The range of variation of boundary values of atomic relations among the basic components - C, H, O, and N - is not infinitely broad. Moreover, it correlates with the source of HS: the maximal content of oxygen and, hence, of oxygen-containing functional groups is encountered in HS from waters. Oxygen content decreases according to this sequence of sources: water, soil, peat, and, finally, coal. On the contrary the concentration of aromatic carbon increases in accordance with this series [2, 4].

Moreover, notwithstanding their origins, all HS are based on the same structural principle: they consist of a carcass – i.e. an aromatic carbon skeleton substituted by alkyl and other functional groups, mainly carboxyl, hydroxyl and methoxyl groups – and of a periphery, rich in polysaccharidic and polypeptidic fragments. For this reason, HS occupy one of the highest positions in structural complexity in the hierarchy of natural organics; far ahead of oil, lignins and coals.

To solve the problem of a quantitative description of the HS structure and properties we have proposed an approach based on the following assumption: *the structure of polydisperse compounds with a non-stoichiometric composition can be characterized by a set of parameters that include atomic relations of the constitutional elements and their distribution along the basic structural fragments* [8].

In our researches we identified some descriptors of HS composition that ensure a maximal discriminating capability for the classification, including a “source of origin” and “fractional composition”, which meet the criteria of fundamentality, reproducibility, and specificity.

Thanks to their structural complexity, HS are capable of a unique variety of interactions, especially their most reactive part: the humus acids. Such groups as carboxyl, hydroxyl and carbonyl in combination with aromatic structures provide humus acids with an ability to enter ionic and donor-acceptor reactions, form hydrogen bonds and actively participate in sorption processes. For instance, humus acids are capable of effective water binding, ion exchange, formation of complexes with metals and of adducts with various classes of organic compounds.

The above properties allow HS to perform a broad set of important biosphere functions, e.g. a structure-forming role in soil [9, 10], accumulation of nutrients and microelements readily assimilable for plants [11], regulation of geochemical metal flows in water and ground ecosystems [4, 12-14]. In the end of the 20th century, when chemical environmental pollution became a widespread problem, they acquired a protective function as well. This action of humus acids bases on their capacity to bind into strong complexes both metal ions and organic ecotoxicants, in polluted water and ground systems [4]. Environmental effects of such binding are exhibited in modification of ecotoxicant forms and migration ability [15], reduction of bioavailability [16, 17], and toxicity [18]. The latter is fundamental because toxic activity is a specific feature of a molecule, that is generally lost or minimized if the molecule is bounded. Thereby humus acids are considered to be natural detoxicants.

Thus, it is impossible to design models of biogeochemical cycles of contaminants and make prognostic assessments of their risk, accumulation rate, and lifetime in the environment, without considering their interactions with humus acids, which radically change chemical and toxicological behaviour of ecotoxicants. This stands for an urgent need in attaining quantitative characteristics of humus acid interactions with diverse ecotoxicants.

Chemists equipped with novel instrumental methodologies met a new social order with enthusiasm. Only in 1999, *Chemical Abstracts* reviewed more than 1200 papers where the structure and properties of humus acids were addressed to that or another extent. As a result, today a huge experimental material has been collected. It should be pinpointed that, along with theoretical studies, researches dealing with new HS applications are growing in number.

## SOURCES AND PREPARATION OF HUMIC SUBSTANCES

The ranking of the sources of humic substances according to their increasing HS content is the following: sea water (up to 1 mg/l), river water (up to 20 mg/l), swamp water (up to 300 mg/l), ground (1-12%), peat (up to 40%), and brown coal (up to 85%) [4]. The highest extracted amounts (up to 85%) of HS represented by humic and fulvo acid fractions (HA and FA, respectively) are found in a brown coal species, namely ‘leonardite’ [19]. Therefore the latter is used for preparation of HS [19-21]. Additional benefits of leonardite relate to its presence in the majority of brown coal deposits [19]. Furthermore, due to its low calorific value, it is often discarded. So the main source of humic substances comes from production tailings of brown coal, in full accordance with green chemistry principles. Note that global brown coal reserves comprise more than 1 trillion tons [22].

Another HS source is sapropel. Only in Russia its resources are estimated at 225 billion $m^3$. Sapropel however contains much more mineral admixtures than leonardite and its chemical composition is more diverse, therefore it needs more sophisticated reprocessing technologies. Nevertheless, sapropel is practicable as a raw material for local industries. In addition, it often includes various microelements useful as fertilizing and fodder additives. Moreover, sapropel recovery allows clearing of silt-up lakes [23], enhancing ecological functions which need light.

Finally, the third HS source is peat. Its world resources exceed 500 billion tons [24]. Since peat extraction damages natural swamps, which play a critical role in environmental balancing, such activity was internationally recognized as unsuitable. Yet in Russia, it is practiced intensively and in some economically depressed regions it is the only source of subsistence for local communities. Peat is mainly used as fuel and local fertilizer, so a switch of peat streams to HS production would allow more rational utilization of this unique natural resource. Even if, from the green chemistry viewpoint, peat is not a suitable HS source, its short-term use for extraction of HS may be practicable.

A basic method of HS separation is alkaline extraction by ammonia, potassium solutions, or sodium hydroxide [25]. Under proper conditions, complete extraction of HS with weak alkaline solution is feasible. This technology is actually waste-free and therefore extensively practiced both in Russia and worldwide. An alternative is mechanical crushing of leonardite with potash, which yields solid water-soluble HA [19].

## APPLICATIONS OF HUMIC SUBSTANCES

Here follows a list of the few HS applications presently existing.

❑ HS capacity to bind metal ions and organic compounds allows their use as:

- ligands in production of microfertilizers, fodder and food additives containing microelements;
- enterosorbents in veterinary (*Gumadapt*, EST-1) and medicine (*Gumivit*);
- neutralizing agents for polluted areas [26, 27].

❑ HS surfactant properties make them usable:

- as drilling mud ingredients (*Polygum-K, Polygum-K1*);
- as ingredients of starch-based sizing formulations for reducing starch concentration and raising efficiency of cotton textile sizing;
- in the form of additives to iodine solutions used as an alternative to cyanic solvents for leaching of materials containing fine-dispersed gold;
- for removal of aromatic hydrocarbons from oil-contaminated aquifers [28].

❑ HS interaction with mineral particles producing in organo-mineral complexes determines their application as soil structure builders and reclamation agents.

❑ HS biological activity permits to apply them as:
- plant growth stimulants (*Lignogumat, Gumat, Gumak*, etc.);
- non-specific adaptogens and biogenic stimulants in medicine (*Gumizol, Triactiv*).

Most extensively HS are applied in plant cultivation as growth stimulants or microfertilizers. In Russia, *Gidrogumat, Oxigumat, Gumoxin-J* and *Sodium Humate* have been officially registered and recommended for application as growth modulators and substances enhancing resistance to diseases (primarily of mycotic origin) and adaptability to adverse weather conditions. Unlike similar synthetic growth modulators, the effect of humic agents is not limited to metabolism. When applied systematically, it improves the structure of soil, adds buffering and ion exchange properties, and stimulates the activity of soil microorganisms.

Lately great attention was given to organo-mineral microfertilizers based on HS, namely potassium and/or sodium humates, with chelated microelements (e.g. Fe, Cu, Zn, Mn, Mo, Co, and B). These are, for instance, *Gumat*+7 and *Gumat-Universal*. These compounds are especially beneficial for carbonate grounds where microelements are scarcely accessible for plants, despite their high gross concentrations. In order to add microelements to soils, the commonly used amendants exploit various synthetic metal chelants like EDTA (ethylenediaminetetraacetate), DTPA (diethylenetriaminepentaacetate), and EDDHA (ethylenediaminedi(o-hydroxyphenylacetic) acid) [29, 30]. Although the synthetic ligand-based fertilizers are highly effective, their production and use entail a series of negative environmental effects. Their industrial synthesis is based on monochloroacetic acid and ethylene diamine obtained from chlorinated hydrocarbons. These congeners pose high risk for humans and the environment. In addition, a regular introduction of synthetic metal-binding agents as fertilizers leads to their accumulation in soil, with a negative impact on its properties. Thus, the production and use of fertilizers based on HS instead of synthetic chemicals may become an environmentally-safe alternative.

Another attractive area of HS applications is remediation of polluted sites. As already mentioned, the range of HS interactions is unique. Such groups as carboxyl, hydroxyl and carbonyl in combination with aromatic structures provide humus acids with an ability to enter ionic and donor-acceptor reactions, form hydrogen bonds and actively participate in sorption processes. Additionally, HS are capable of the ion exchange, formation of complexes with metals and of adducts with various classes of organic compounds. Binding of toxicants leads to reduction of their free form concentration and, as a result, to a toxicity drop. Therefore HS act as natural detoxifying agents and thereby they have potential for remediation of lands polluted by organics contaminants [31], including polynuclear aromatic hydrocarbons [28], oil products [32, 33], and heavy metals [34, 35]. HS-based solid sorbents – designed for superficial and ground water treatment – were already developed and used abroad [27].

Apart from being binders, HS possess explicit surfactant properties, which enable their use for increasing solubility of hydrophobic organic compounds, including oil products. HS may serve as a basis for solutions designed for flushing of aquifers contaminated with aromatic organics. Opposite to synthetic surfactants usually employed for this purpose, the HS preparation does not involve toxic substances. In addition, humic agents are not xenobiotics, so they present a limited environmental impact.

Other HS applications, including medical ones, are not common. To a great extent, this is due to the heterogeneity of the HS structure, which is responsible for both a broad range of HS properties and non-specificity of their action. So, for remediation of environments polluted with hydrophobic compounds it is preferable to employ HS with a higher affinity to the above contaminants, i.e. HS should be characterized by pronounced hydrophobic features. Alternatively, when used for microfertilizers, requested HS features are high solubility and abundance of functional groups. Thus HS targeted modification, leading to preparation of agents with predefined properties, is the critical target to be attained for increasing efficiency of humic agents in a specific area and generally extending the range of their applications.

## CHEMICAL MODIFICATION OF HUMIC SUBSTANCES AS A PROMISING PATHWAY FOR EXTENSION OF THEIR APPLICATIONS

A possible method for the preparation of humic agents with pre-set properties is chemical modification. By now, we have examined two HS modification types described below.

### HS SULFONATION FOR INCREASING SOLUBILITY OF THEIR COMPLEXES WITH METALS.

As mentioned above, HS-based microfertilizers represent one of the most promising HS applications. However, solubility of HS complexes with metals is lower than that of their synthetic chelating analogues, this considerably hampers their practical utilization. For such application of HS, it is important to find a way to increase solubility of both humic agents and their complexes with metals. We proposed a modification based on the introduction of additional $SO_3H$ groups to the HS structure, in order to enhance their solubility and metal-binding capacity. Sulphuric and chlorosulphonic acids were employed as sulphonating agents.

As shown by experimental data, HS sulphonation led to an augmented solubility in the prepared samples [36]. In parallel, the modified samples were characterized by a major number of metal-binding centres. The latter was tested assessing HS binding capability of $Fe^{3+}$, which was increased from 1-2 to 2-4 mmol/g HS. Thus we have shown that sulfonation is a promising way of HS modification for increasing solubility of HS complexes with metals.

## ACIDOLYSIS OF HUMIC SUBSTANCES

The HS structure is characteristic of the presence of two building blocks, which mainly differ in their chemical nature and traditionally defined as an "aromatic carcass" and a "carbohydrate-peptide periphery" [4]. Such differentiation bases on the HS hydrolytic elimination results, they prove the existence of a "non-hydrolysable" part (carcass) and an "hydrolysable" one (periphery) in the HS molecular complex. HS reactivity is changing depending on the prevalence of either the aromatic carcass or periphery. So, the possibility of differential and controlled hydrolysation of the two HS parts is fundamental for preparation of humic agents with targeted action.

To this purpose, we have carried out a hydrolysis of a number of HA samples and the characterization of its products. The hydrolysis occurred under relatively mild conditions (0.2M HCl; T=110°C; 20 hours), in order to eliminate only the peripheral carbohydrate fragments without changing the aromatic carcass. The analysis of the hydrolysis products has shown that the carbon content in modified HA enriched with the carcass fragments is higher than in initial HA and the H/C and O/C ratios are significantly lower. Thus we demonstrated that aliphatic oxygen containing fragments split off from HA during the hydrolysis [37].

For characterizing reactivity of the starting HA and products of their hydrolysis, we determined constants of their binding with pyrene – a contaminant from polynuclear aromatic hydrocarbons (PAH) – using a method of fluorescence quenching.

The experimental results have shown that the constant of binding with pyrene increases in the HA hydrolyzed samples enriched with the carcass fragments. After hydrolysis, the values of the binding constant were 20% higher on average, than in the raw samples. Our results support that the degree of aromatic fragments concentration in HA is fundamental for their affinity to PAH.

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*This paper does not cover the entire accumulated data on existing HS application technologies and opportunities. Recent publications offer a great number of original solutions regarding new potential applications of humic substances. This is a clear evidence of a growing significance of these unique substances, which both play an important role in all biosphere processes and create optimal environmental conditions for the existence and evolution of life.*

## REFERENCES

1. HEDGES J.I., J.M. OADES Org. Geochem., 1997, 27, pp. 319-361.
2. ORLOV D.S. Humus Acids of Soils and General Theory of Humification. MSU, M., 1990, 325p.
3. STEVENSON F.J. Humus Chemistry, Genesis, Composition, Reactions. John Wiley&Sons, New York, 1982, 443p.
4. ORLOV D.S. Soil Chemistry. MSU, M., 1992, 259p.
5. AHARD F. Grell's Chem. Ann., 1786, 2, p.391.
6. VARSHAL G.M., VELUKHANOVA T.K., KOSCHEEVA I.YA. Geochemical role of humus acids in elements migration. In: Humic Substances in Biosphere, Nauka, M., 93, pp.97-116.
7. KLEINHEMPEL D. Albrecht-Thaer-Archiv., 1970, 14(1), pp.3-14.
8. PERMINOVA I.V. Analysis, Classification and Forecast of Properties of Humus Acids. D.Sc. Thesis, 2000, Moscow.
9. MARTIN J.P. and WAKSMAN S.A. Soil Sci., 1941, 52, pp.381-394.
10. CHANEY K. and SWIFT R.S. J. Soil Sci., 1984, 35, pp.223-230.
11. TATE R.L. Adv. Microbial. Ecol., 1980, 4, pp.169-201.
12. VARSHAL G.M., VELUKHANOVA T.K., SIROTKINA I.S. et al. Hydrochem. Materials, 1973, 59, pp.143-151.
13. VARSHAL G.M., KOSCHEEVA I.YA., SIROTKINA I.S. et al. Geochemistry, 1979, 4, pp.598-607.
14. LINNIK P.N., NABIVANETS B.I. Forms of Metal Migration in Sweet Surface Waters. L., Gidrometeoizdat, 1986, 268p.
15. VARSHAL G.M., BUACHIDZE N.S. J. Anal. Chem., 1983, 38(12), pp. 2155-2167.
16. LANDRUM P.F, SHEILA R.N, EADIE B.J, HERCHE L.R. Environ. Toxicol. Chem., 1987, 6, pp.11-20.
17. BLACK M.C. and MCCARTHY J.F. Environ. Toxicol. Chem., 1988, 7, pp.593-600.
18. BOLLAG, J.-M. and K. MAYERS Sci. Total Environ., 1992, 117/118, pp.357-366.
19. Biopolymers, Lignin, Humic Substances and Coal Hofrichter M., Steinbuechel (Eds.), Wiley-VCH, 2001, 523p.
20. Conversion and Utilization of Waste Materials (Applied Energy Technology Series) M.R. Knan (ed.), Taylor & Francis, June 1996, 286p.
21. LEVINSKY B.V. Everything about Humates. Irkutsk, 2000.
22. THOMAS L. Coal Geology, John Wiley & Sons, 2002, 396p.
23. VLASOV B.P., GIGEVICH G.S., KARTASHEVICH Z.K., and PRYTKOVA M.Ya./Actions for lake ecosystems remediation: onsite activities. In: Remediation of Small Lakes Ecosystems. S.-Petersburg, Nauka, 1991.
24. MARKOV V.D., OLUNIN A.S, OSIPENKOVA L.A., SKOBEEVA E.I., KHOROSHEV P.I. World Peat Reserves. M., Nedra, 1988.
25. Humic Substances and their Role in the Environment Frimmel F.H., Christman R.F (Eds.), John Willey&Sons, 1988.
26. SCHWARTZ D.L. Solid waste and emergency response (5102G), EPA 542-N-99-002. 31, 1, 1999.
27. SANJAY H.G., SRIVASTAVA K.C., WALIA D.S. Mixed Waste Remediation Using HUMASORB-CSTM - an Adsorbent to Remove Organic and Inorganic Contaminants. ARCTECH, Inc., 1997.
28. LESAGE S., NOVAKOWSKI K.S., BROWN S., MILLAR K. J. Environ. Sci. Health A, 2001, 36(8), pp. 1515-1533.
29. HAVLIN J.L., TISDALE S.L., NELSON W.L., BEATON J.D. Soil Fertility and Fertilizers: An Introduc-

tion to Nutrient Management (6th Edition), Prentice Hall, 499p., 1998.

30. Goos R.J., Johnson B. Agr. J., 2000, 92, pp.1135-1139.
31. Fukushima M., Tatsumi K. Analyt. Sci., 2001, 17, pp. i821-i823.
32. Molson J.W., Frind E.O., Van Stempvoort D.R., Lesage S. J. Contam. Hydrol., 2001, 54, pp. 277-305.
33. Salem K.M., Perminova I.V., Grechischeva N.Yu. Murygina V.P., Mescheryakov S.B. In: Environment and Industry of Russia, 2003, pp.19-21.
34. Iljin V.B.. Heavy Metals in the System "Soil-Plant". Novosibirsk, Nauka, 1991.
35. Sawada A., Tanaka S., Fukushima M., Tatsumi K. J. Hazard. Mater., 2003 (B96), pp. 145-154.
36. Youdov M.V., Perminova I.V., Pankova A.P., Zhilin D.M., Gantman M. In: Abstracts of NATO Advanced Research Workshop: “Use of humates to remediate polluted environments: from theory to practice”, September 23-29, 2002. Zvenigorod, Russia. pp. 34-35.
37. Youdov M.V., Kovalenko A.N., Perminova I.V., Petrosyan V.S. In: Abstract Book of the 2nd International Congress: “Biotechnology: State of the Art and Prospects of Development”. Nov. 10-14, 2003. Moscow, Russia.

# DISPOSAL OF ELECTRIC TECHNOLOGICAL FLUIDS CONTAINING POLYCHLORINATED BIPHENYLS (PCB)

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## INTRODUCTION

The Stockholm Convention on the Destruction of Persistent Organic Pollutants (POPs) demands full destruction of the twelve most dangerous POPs, including polychlorinated biphenyls (PCBs). Russia signed the Convention in May 2002. PCBs are used as basic ingredients in some transformer oils, condenser oils, as hydraulic fluids (this practice is unavailable in Russia), etc. PCBs are synthesized by direct biphenyl chlorination, due to such process they are marketed as blends, which may contain more than 200 types of PCB isomers and congeners (homologues).
General PCB formula

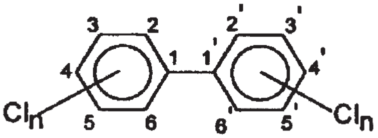

**Fig. 1. Hypothetic structural fragment of humus acids in soils [7].**

## PROPERTIES OF COMMERCIAL PCB BLENDS

Commercial PCBs are transparent, viscous, colourless or yellowish liquids. The physico-chemical properties of commercial PCBs are determined by the composition of their ingredients and chlorine concentration.

Commercial PCB formulations are represented by a variety of trade names, e.g. *Arochlor* (USA), *Phenochlor* (France), *Chlophen* (Germany), *Kanechlor* (Japan), *Fenclor* (Italy), *Sovol* (USSR, Russia), etc. Some PCB products from the United States, namely the *Arochlor* ones, are identified by a numeric code, e.g. *Arochlor* 1254 or *Arochlor* 1248, where the digit "12" indicates the number of carbon atoms in biphenyl and the last two digits correspond to the chlorine percentage in the product.

In the USSR, different PCB blends were manufactured for technological applications, among them:

- *Trichlorodiphenyl* (a mixture of 85% *Sovol* and 15% α-nitronaphthaline);
- *Sovol* (a mixture of tetra- and pentachlorobipnenyls);
- *Sovtol* (*Sovol* and trichlorobenzene). Variants: *Sovtol*-1 (75% *Sovol* and 25% trichlorobenzene), *Sovtol*-2 (64% Sovol and 36% trichlorobenzene), and *Sovtol*-10 (90% *Sovol* and 10% trichlorobenzene);
- *Nitrosovtol* (92.5% Sovol and 17.5% α- nitronaphthaline);
- *Hexol* (pentachlorobiphenyl with hexachlorobutadiene).

The properties of some of these oils are provided in published handbooks [1, 2].

- Sovol, plasticizer – a colorless liquid, purified mixture of biphenyl polychlorides. Viscosity according to Oswald-Pinkenitch: 25-35 centistokes at 65°C. Density: 1.47-1.51 g/cm$^3$ at 60°C. Flash point: minimum 190°C. Congelation point: maximum 9°C. VOC (volatile organic compounds) concentration (for 6 h at 100°C): not more than 0.2%. No contaminants. Acidity index: not higher than 0.03 mg KOH per 1 g of *Sovol*.
- *Sovol, insulating fluid* – a transparent colourless or yellowish liquid, without contaminants. Special-purity grade product, the mean composition corresponds to pentachlorobiphenyl. Viscosity according to Oswald-Pinkenitch: 35 centistokes at 65°C. Density: 1.455-1.515 g/cm$^3$ at 60°C. Flash point: minimum 200°C. Congelation point: maximum 6°C. Acidity index: not higher than 0.015 mg KOH per 1 g of *Sovol*. Mobile chlorine concentration: not more than 0.1%. Permittivity: not less than 4.8 at 20°C and 4.1 at 90°C.
- *Sovtol-10* – a transparent colourless or yellowish liquid, contaminants- and water-free, a mixture of purified pentachlorobiphenyl (Sovol, insulating) and trichlorobenzene. Kinematic viscosity: 14 centistokes at 65°C. Acidity index: 0.02 mg KOH per 1 g.

## THE INVENTORY OF PCB IN RUSSIA [3]

A larger part of PCB-containing equipment (20%) is used in Russian energy systems. A similar portion (18%) is used for mechanical and instrument engineering industries, 14% for ferrous and nonferrous metallurgic sectors, 10% for food industry, and 9% for chemical industry.

PCB-containing equipments are operated at more than 1,000 productive sites countrywide. In Russia there are about 200,000 transformers and condensers (counting both active and inactive ones), more than 18,000 use PCB-based oils (*Sovol* and *Sovtol*). According to different estimates, the total quantity of PCBs stocked in Russia ranges from $10^4$ to $10^5$ tons.

## PCB HAZARD

The inclusion of PCBs in list of the Stockholm Convention is motivated by their high toxicity, stability, and tendency to bioaccumulation [4].

PCBs produce acute impact on water organisms at concentrations above 1 mg/l. Fish die at an *Arochlor*-1254 concentration of 5 μg/l. $LDs_{50}$ for rats vary from 4.0 to 11.3 g/kg. *Sovol* vapors in a concentration 10 mg/l kill white rats after 3 hours of exposure. The overall toxicity of PCB mixtures is both related to the general dangerousness of the PCB molecules and the specific toxicity of single congeners. All planar and mono-*ortho*-substituted PCB congeners, similar to lateral-substituted dibenzodioxins and furans, interact with Ah-receptors (Ah, acronym from Aryl hydrocarbons) of the cell resulting in heavy affections of all aerobic organisms. According to this feature, PCB congeners are split into three categories:

- moderately toxic PCBs, molecules which cannot acquire a planar configuration;
- highly toxic PCBs:
  a) without substituents in the *ortho*-position (non-*ortho*)
  b) with only one chlorine atom in the *ortho*-position (mono-*ortho*).

Table 1 lists toxicity factor of some PCB congeners compared to 2,3,7,8-tetrachlorodibenzo-*para*-dioxin (TCDD), which was assigned toxicity equal to 1, on the basis of its maximum toxicity among the congeners.

**Table 1. International toxicity factors for PCB congeners.**

| IUPAC nomenclature (number) | Congener structure | Toxicity factor WHO-TEF (1997) |
|---|---|---|
| *Group of PCB congeners without a substituent in the* ortho-*position* | | |
| PCB 77 | 3,3’,4,4’-TCB | 0.0001 |
| PCB 81 | 3,4,4’,5-TCB | 0.0001 |
| PCB 126 | 3,3’,4,4’-PeCB | 0.1 |
| PCB 169 | 3,3’,4,4’,5,5’-HxCB | 0.01 |
| *Group of mono-*ortho-*substituted PCB congeners* | | |
| PCB 105 | 2,3,3’,4,4’-PeCB | 0.0001 |
| PCB 114 | 2,3,4,4’,5- PeCB | 0.0005 |
| PCB 118 | 2,3’,4,4’,5- PeCB | 0.0001 |
| PCB 123 | 2’,3,4,4’,5- PeCB | 0.0001 |
| ??? 156 | 2,3,3’,4,4’,5-HxCB | 0.0005 |
| PCB 157 | 2,3,3’,4,4’,5’-HxCB | 0.0005 |
| PCB 167 | 2,3’,4,4’,5,5’-HxCB | 0.00001 |
| PCB 189 | 2,3,3’,4,4’,5,5’-HpCB | 0.0001 |

In addition to highly-toxic PCB congeners, technological blends contain polychlorinated dibenzo-*para*-dioxins (PCDD) and furans (PCDF) in hazardous amounts.

The toxicity of transformer oils ranges in the order of 10,000 toxic equivalents (ng WHO-TEQ/g) (see Table 3) posing an extreme risk to environment and health. Contamination occurs both when such oils evaporate during their use and storage, or when they are spilled as a result of accidents or negligent storage.

## CHARACTERIZATION OF TRANSFORMER OILS MANUFACTURED IN RUSSIA

A bulk of PCB oils used for electric applications has been stored or present in operating equipment for a few decades. Specialists from NPO *Taifun* carefully studied three samples of such oils. The samples designated as O1 and O2 represent transformer oils of the *Sovtol*-10 mark. The former was manufactured in 1979 and the latter was loaded into the transformer in 1976. The sample O3 was taken from a high-capacity condenser, currently deactivated. The date of its manufacture is unknown, though lifetimes of such condensers are estimated at about 20 years. The collected data are reported in Tables 2 to 4. The samples are typical for Russian (and CIS) dielectric oils both stored in depots and currently loaded in electric machineries.

**Table 2. PCB congener composition (concentrations) in three samples of Russian electric oils. Data are arranged according to the elution order from the chromatographic column. The concentrations are expressed in μg of PCB per g of oil.**

| PCB congeners | O1 | O2 | O3 | PCB congeners | O1 | O2 | O3 |
|---|---|---|---|---|---|---|---|
| #6 [Cl 2] | 31 | 213 | 5,801 | #151 [Cl 6] | 2,222 | 3,026 | 231 |
| #8 [Cl 2] | 381 | 996 | 38,015 | #135 [Cl 6] | 2,851 | 3,750 | 120 |
| #19 [Cl 3] | - | - | - | #149 [Cl 6] | 15,257 | 18,017 | 1,260 |
| #17/#18 [Cl 3] | 286 | 1,013 | 50,795 | #118 [Cl 5] | 45,913 | 39,421 | 4,079 |
| #15 [Cl 2] | 208 | 293 | 9,311 | #146 [Cl 6] | 2,571 | 3,083 | 228 |
| #24/#27 [Cl 3] | - | - | 3,124 | #153 [Cl 6] | 30,161 | 30,087 | 1,828 |
| #16 [Cl 3] | 259 | 608 | 34,397 | #105 [Cl 5] | 21,173 | 21,277 | 2,176 |
| #26 /25 [Cl 3] | 76 | 258 | 9,727 | #141 [Cl 6] | 3,559 | 4,437 | 129 |
| #28/31 [Cl 3] | 1,534 | 2,313 | 45,073 | #138 [Cl 6] | 41,306 | 40,225 | 2,715 |
| #33 [Cl 3] | 232 | 787 | 26,137 | #126 [Cl 5] | 111 | 110 | - |
| #22 [Cl 3] | 128 | 615 | 14,610 | #187 [Cl 7] | 671 | 984 | - |
| #45 [Cl 4] | 112 | 224 | 3,414 | #183 [Cl 7] | 720 | 759 | - |
| #52 [Cl 4] | 20,843 | 25,967 | 13,600 | #128 [Cl 6] | 9,563 | 9,329 | 630 |
| #49 [Cl 4] | 3,421 | 3,519 | 5,442 | #167 [Cl 6] | 1,564 | 1,428 | 100 |
| #47 [Cl 4] | 1,829 | 1,575 | 8,640 | #174 [Cl 7] | 725 | 1,013 | - |
| #44 [Cl 4] | 9,718 | 12,087 | 18,189 | #177 [Cl 7] | 842 | 1,207 | - |
| #37 [Cl 3] | 140 | 331 | 9,308 | #171 [Cl 7] | 658 | 934 | - |
| #41 [Cl 4] | 4,808 | 7,055 | 16,864 | #156 [Cl 6] | 3,901 | 3,387 | - |
| #74 [Cl 4] | 6,869 | 6,553 | 5,858 | #201 [Cl 8] | 6,682 | 6,754 | 342 |
| #70 [Cl 4] | 19,859 | 23,075 | 14,106 | #157 [Cl 6] | 1,555 | 1,518 | 0 |
| #66 [Cl 4] | 11,609 | 6,784 | 10,591 | #180 [Cl 7] | 2,767 | 3,214 | 94 |
| #95 [Cl 5] | 19,383 | 23,354 | 3,227 | #170 [Cl 7] | 2,495 | 2,977 | 85 |
| #60 [Cl 4] | 4,275 | 4,670 | 9,222 | #169 [Cl 6] | 103 | 128 | - |
| #84 [Cl 5] | 4,234 | 8,223 | 1,125 | #199 [Cl 8] | 89 | - | - |
| #101 [Cl 5] | 25,958 | 28,667 | 3,351 | #196/203 [Cl 8] | 108 | - | - |
| #99 [Cl 5] | 21,846 | 10,717 | 1,789 | #189 [Cl 7] | 76 | 112 | |
| #97 [Cl 5] | 12,874 | 14,488 | 1,579 | #195 [Cl 8] | - | - | - |
| #87 [Cl 5] | 14,553 | 17,482 | 2,097 | #207 [Cl 9] | - | - | - |
| #136 [Cl 6] | 2,175 | 2,784 | 200 | #194[Cl 8] | - | - | - |
| #110 [Cl 5] | 35,798 | 29,135 | 4,776 | #205[Cl 8] | - | - | - |
| #77 [Cl 4] | 201 | 318 | 1,524 | #206[Cl 9] | - | - | - |
| | | | | #209[Cl 10] | - | - | - |

Note: Mono-*ortho* PCBs 114, 122, 123, and 124 were identified using a special analytical technique. Those isomers are seldom encountered in notable quantities. The same refers to PCB 81 that is about equal in quantity to PCB 77.

Oil toxicity is rather high. Particularly, O1 is characterized by toxicity of 12.5 μg WHO-TEQ/g, which is singularly due to the presence of di-*ortho*-congeners PCB 77, 126 and 169; plus a contribution of 7.2 μg WHO-TEQ/g given by mono-*ortho*-congeners. So, its total toxicity reaches 19.7 mg WHO-TEQ/g (the WHO-TEF scale takes into account only carcinogenic risk for humans). However, in addition to the toxicity associated with PCBs, such oils are contaminated with polychlorinated dibenzo-*para*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) collectively called “dioxins”.

Table 3 shows the data on contamination of oils by dioxins. Toxicity is mainly caused by PCDF. Total toxicity of the oils due to dioxins/furans is very high, e.g. in O1 it reaches 13.27 g WHO-TEQ/ton of oil. In order to get a term of comparison, we can note that overall Russian emissions are estimated at approximately 10 kg WHO-TEQ per year [5] and air emissions in the Netherlands reach about 400 g WHO-TEQ per year. Thus the sole O1 type transformer oils, which total amount is estimated in 20,000 tons, contains almost 300 (265.4) kg WHO-TEQ of dioxins. From these data is evident that there is an urgent need for neutralization of such oils.

**Table 3. Polychlorinated dibenzo-*para*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) quantities in three transformer oil samples.**
**(Toxicity was evaluated by WHO-TEF, 1997).**

| **PCDD/PCDF congeners** | ***Sovtol*** **O1** | | ***Sovtol*** **O2** | | ***Sovtol*** **O3** | |
|---|---|---|---|---|---|---|
| | *ng/g* | *TEQ ng/g* | *ng/g* | *TEQ ng/g* | *ng/g* | *TEQ ng/g* |
| 2378 TCDD | 14.3 | 14.3 | 28.7 | 28.7 | 2.56 | 2.56 |
| 12378 PeCDD | 30.6 | 30.6 | 58.3 | 29.15 | 0.98 | 0.49 |
| 123478 HxCDD | 12.4 | 1.24 | 32.2 | 3.22 | 0.34 | 0.034 |
| 123678 HxCDD | 10.6 | 1.06 | 24.4 | 2.44 | 0.22 | 0.022 |
| 123789 HxCDD | 8.6 | 0.86 | 30.4 | 3.04 | 0.36 | 0.036 |
| 1234678 HpCDD | 8.5 | 0.085 | 17.6 | 0.176 | 0.20 | 0.002 |
| OCDD | 3.20 | 0.0032 | 4.5 | 0.0045 | 0.15 | 0.00015 |
| 2378 TCDF | 2049 | 204.9 | 5,392.0 | 539.2 | 119.4 | 11.94 |
| 12378 PeCDF | 11,381 | 569.05 | 23,497.0 | 117.485 | 26.15 | 1.307 |
| 23478 PeCDF | 15,032 | 7516 | 44,060.0 | 22030.0 | 160.9 | 80.45 |
| 123478 HxCDF | 19,284 | 1,928.4 | 48,808.0 | 4880.8 | 34.8 | 3.48 |
| 123678 HxCDF | 5,002 | 500.2 | 11,142.0 | 1114.2 | 12.2 | 1.22 |
| 234678 HxCDF | 7,296 | 729.6 | 1,119.0 | 111.9 | 12.1 | 1.21 |
| 123789 HxCDF | 17,089 | 1,708.9 | 39,450.0 | 3945.0 | 16.6 | 1.66 |
| 1234678 HpCDF | 2,161 | 21.61 | 6,133.0 | 61.33 | 10.2 | 0.102 |
| 1234789 HpCDF | 5,667 | 56.67 | 14,492.0 | 144.92 | 5.56 | 0.0556 |
| OCDF | 894 | 0.0894 | 2,100.0 | 2.1 | 4.7 | 0.0047 |
| ∑ TEQ | | 13,283.6 | | 35,872.614 | | 105.191 |
| ∑ TCDF | 4,119 | | 16,565.0 | | 5,588.0 | |
| ∑ PeCDF | 19,742 | | 61,540.0 | | 801.4 | |
| ∑ HxCDF | 10,414 | | 32,037.0 | | 47.4 | |
| ∑ HpCDF | 7,028 | | 11,643.0 | | 6.8 | |
| ∑ TCDD | 32.84 | | 32.8 | | 8.1 | |
| ∑ PeCDD | 26.75 | | 26.7 | | 2.3 | |
| ∑ HxCDD | 13.6 | | 30.5 | | 1.2 | |
| ∑ HpCDD | 6.8 | | 12.6 | | 0.9 | |

Table 4 reports data on the group composition of oils analyzed for dioxins (Table 3). Samples O1 and O2 are close in composition to oils of the *Arochlor* 1254 series, these types of oils are mainly used in transformers. The sample O3 is close to *Arochlor* 1242, commonly used for condenser filling.

**Table 4. Group compositions of the studied *Sovols*. Integral chlorine is reported in mg/g and in % w/w.**

| Group | O1 | % | O2 | % | O3 | % |
|---|---|---|---|---|---|---|
| ∑ **Cl 2** | 0.76 | 0.1 | 2.97 | 0.5 | 86.3 | 20.2 |
| ∑ **Cl 3** | 2.65 | 0.5 | 5.77 | 1.0 | 196 | 45.9 |
| ∑ **Cl 4** | 87.9 | 15.6 | 100 | 17.7 | 108 | 25.3 |
| ∑ **Cl 5** | 322 | 57.1 | 290 | 51.2 | 27.0 | 6.3 |
| ∑ **Cl 6** | 141 | 25 | 155 | 27.4 | 9.20 | 2.2 |
| ∑ **Cl 7** | 9.44 | 1.7 | 11.3 | 2.0 | 0.18 | 0.04 |
| ∑ **Cl 8** | 0.20 | 0.04 | 0.15 | 0.03 | - | |
| **Total** | **564** | | **566** | | **427** | |

It is clear that the whole technological oil mixture must be destroyed. In fact it is impossible to selectively eliminate only the toxic congeners, since all those chlorinated molecules have similar physico-chemical properties. Additionally, destruction of toxic dioxins/furans must be assured as well.

## HYDRODECHLORINATION OF PCBS IN TECHNOLOGICAL (DIELECTRIC) OILS

Multiple efforts were made in many countries to destroy POPs, but no universal method – applicable to all POPs – is so far available.

A well-developed technology for destroying organochlorine toxicants, including PCBs, is Gas-Phase Chemical Reduction (GPCR) proposed by *ELI Eco Logic International Inc.* [6]. The EcoLogic system has been operated in Australia for several years. About 2.5 thousand tons of POPs, PCBs included, were destroyed over this period. Reduction of organochlorine compounds (POPs) is carried out using hydrogen at a temperature of 850°C or higher. An important feature, that distinguishes this technology from other methods, is the use of a water decomposition reaction at high temperatures for hydrogen regeneration. This technique helps avoid drying of POP mixtures or POP-polluted matters (soils, sediments, etc.). The key fault of EcoLogic is the risk of explosion, due to the usage of hydrogen at very high temperatures.

Back in 1994, P. Tundo and his co-workers successfully experimented hydrodechlorination (HDC) of PCBs [7]. Their results were confirmed by other PBC HDC researchers. The major conclusion was that the PCB HDC alternative is very useful for PCB destruction. Both the reaction selectivity and the kinetics of chlorine loss in PCB molecules were studied in these researches. The proposed method exploits multiphase catalysis with a palladium catalyst and Aliquat 336®, such process appeared to be efficient, though it required further comprehensive investigations.

A few detailed reviews addressing PCB reactions and methods for their HDC are available in literature [8, 9]. PCB HDC reactions with various hydrogen donors were rather deeply examined. Among the pioneers in this area was V.V. Lunin and his team. In [10], it was shown that HDC can be obtained thanks to the action of isopropyl alcohol, in which hydrogen elimination from the second position takes place. Later, this observation found confirmation in liquid-phase reaction experiments with labelled atoms [11]. However, these results will not be discussed in this paper as they lie outside our research on PCB HDC using hydrogen.

## HDC KINETICS

It is quite challenging to draw an exhaustive picture of congener transformations and transitions in technological oils, because, besides being mixtures, the different PCB congeners are present in varying proportions. Furthermore, separating individual congeners in their pure form is a difficult and very expensive task. For these reasons, kinetic measurements are mostly done for the whole mixtures.

It is not easy to collect and compare the results of kinetics researches as they were performed using different catalysts and conditions. Anyway, some general features can be identified.

In [14], the HDC reaction of *Arochlor* 1240 was examined in a flow system, with coal-supported palladium (0.5%) as catalyst and decahydronaphthaline as a solvent. It was shown that the 100%-conversion of *Arochlor* 1240 was achievable using a sufficient hydrogen excess and appropriate temperatures. Specifically, at the ratio $H_2/Cl = 1.95$, pressure 1 atm and temperature 483K (210°C) the 100%-conversion was reached at moderate velocities. The reaction yields biphenyl as main product, along with cyclohexylbenzene. The authors also studied the influence of alkali additives, as well as issues pertaining to the catalyst regeneration.

The kinetics of 2,4,4',6-tetrachloroBP and 2,3,4,5-tetrachloroBF HDC on the combined catalyst Ni-Mo/$\gamma$-$Al_2O_3$ was analyzed in [15]. The authors determined all velocity constants and concluded that the HDC reaction proceeded by an electrophilic mechanism and that the *ortho*-intermediates were depleted slower than the *meta*- and *para*- ones.

The kinetics of consecutive HDC of a heavier PCB mixture was studied in [16]. The authors outlined that this technology is also practicable for HDC of other chlorine organic compounds such as DDT. The reaction was conducted in dehydrated ethanol. *Arochlor* 1248 (48% Cl) was chosen as PCB mixture. NaOH was used as HCl acceptor and 61% Ni as catalyst on kieselguhr (Girdler G49-A$^{TM}$). The reaction was carried out at temperatures ranging from 60 to 130°C, under an hydrogen pressure minor than 50 atm, with a reaction time of about 20 h. The yield was not specified, though, judging from the reported experimental data, it should be at least 80% at temperatures above 100°C.

In terms of technological feasibility, an advantage of the proposed method is the use of the commercial nickel catalyst and of low-cost alkali. However, this technology is also unsafe as it involves use of hydrogen under a pressure of 50 atm. Significant disadvantages of the process are its long duration and relatively low conversion degree. An appreciable difference was also noted for what concerns the rates of elimination of chlorine from *ortho*- and *meta/para*-chlorine-substituted biphenyls.

Thus the majority of the HDC kinetics data relates to gas-phase processes in flow reactors.

The kinetics of HDC and hydrogenation of chlorinated compounds, including lindane, was examined in aqueous mixtures [12] over a $Pd/Al_2O_3$ catalyst at room temperature, though PCBs were not included in the research.

## HDC RESEARCHES AT ZELINSKY INSTITUTE OF ORGANIC CHEMISTRY RAS

These researches were supported by the INTAS and NATO grants (INTAS No. 2000-00710, NATO No. 977159). Under these projects, PCB hydrodechlorination for electric technological oils was studied, using different solvents and heterogeneous catalysts in a hydrogen atmosphere at room temperature and pressure.

The proposed technology for disposal (or destruction) of polychlorinated biphenyls incorporated in transformer oils consists of oil hydrogenation in the presence of HCl acceptors, i.e. alkaline or alkali-earth hydroxides. The process is implemented in a hydrogen atmosphere using mono- or bimetallic heterogeneous catalysts, supported on noble metals (Pd, Pt) or nickel. Full PCB destruction occurs at room temperature after a period of 30-120 minutes.

This technology is also applicable to chlorinated pesticides and other aliphatic and aromatic chlorinated compounds.

## EXPERIMENTAL

Hydrodechlorination of PCB fluids was carried out in a hydrogen atmosphere at room temperature, using a 10% Pd/C catalyst. Example: 0.224 g (about 0.7 mmol) of PCB and 0.3 g (5.2 mmol) of KOH were dissolved in 10 ml of isopropyl alcohol. Then 0.01 ml of undecane (as GLC standard) and 0.09 g/mol of Pd/C catalyst were introduced into the mixture. The reaction mass was analyzed using a laboratory GL chromatograph and GL-CM Shimadzu GC-MS-QP 5050 A. In some tests also a GC-MS GC 3400 was employed.

**Table 5. Hydrodechlorination of the technological fluid *Trichlorodiphenyl* (an *Arochlor* 1242 analogue) in various solvents.**

| No. | Solvent | Reaction time, min | PCB conversion, % | Biphenyl yield, % |
|---|---|---|---|---|
| 1 | Isooctane | 30 | 30 | 18.5 |
| | | 100 | 100 | 100 |
| 2 | Butanol | 170 | 95 | 74 |
| | | 290 | 100 | 89 |
| 3 | Tret-butanol | 130 | 8 | 4 |
| | | 310 | 30 | 13 |
| 4 | N-butanol | 170 | 95 | 74 |
| | | 290 | 100 | 89 |
| 5 | N-propanol | 20 | 65 | 32 |
| | | 70 | 100 | 96.4 |
| | | 150 | 100 | 100 |
| 6 | Isopropanol | 150 | 100 | 72 |
| | | 330 | 98 | 98 |
| 7 | Ethanol (abs) | 20 | 86 | 60 |
| | | 60 | 100 | 100 |
| 8 | Ethanol (aq.) | 30 | 100 | 100 |
| | | 60 | 100 | 100 |
| 9 | Methanol (abs) | 10 | 28 | 5.5 |
| | | 30 | 100 | 100 |
| 10 | Methanol (aq.) (85%) | 13 | 25 | 10 |
| | | 38 | 100 | 100 |

## RESULTS AND DISCUSSION

### ROLE OF SOLVENTS

The tabulated data (Table 5) indicate that the HDC rate noticeably grows when transiting to more polar alcohols (from butanol to methanol). The addition of water further accelerates the reaction. It was shown in past researches [12, 13] that the HDC reaction could also be conducted in absolute water solutions. Such technologies can definitely reduce the PCB destruction cost, yet certain difficulties with wastewater treatment may arise. Ionic liquids have great potential for the solution of this problem. At present moment, the use of alcohols is still preferred to hydrocarbons for such processes.

In [16] it was shown that the "group rate" of dechlorination was strongly dependent on the number of chlorine atoms involved:

$$ff_5 <1> ff_4 <0.40> ff_3 <0.23> ff_2 <0.36> ff_1 <0.40> ff$$

where $ff$ – is the biphenyl molecule and the digit (0-5) indicates the number of chlorine atoms in the molecule.

In such series we assume that the relative rate constant for the transition from a congener group with five chlorine atoms to a group of tetra-chlorine-substituted congeners is equal to 1. Using the reported values, the transition from trichloro-substituted to dichloro-substituted congeners will be almost four times slower (0.23). Our data indicate that pentachloro-substituted congeners will eliminate chlorine more easily than the ones with minor substitution. We can assume that the most toxic highly-substituted PCB congeners will decay first; in the case of an incomplete conversion, mainly non-toxic mono- and dichloroBP will remain in the final mixture.

**Table 6. Kinetics of changes in PCB congener concentrations in a sample of the technological fluid *Trichlorodiphenyl* under hydrodechlorination in hydrogen flow under alkaline conditions (KOH) at room temperature. Catalyst: 10% Pd/C. Solvent: isopropyl alcohol. Concentrations are expressed in ‰ w/w.**

| **Mass** | **Retention time. min** | **Time, min** | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 30 | 90 | 150 | 210 | 270 | 360 |
| | | Biphenyl | | | | | | |
| 154 | 11.783 | 3.03/**6.29** | 205.93 | 950.78 | 1499.94 | 1837.59 | 1798.6 | 1998.9/<br>**98.69** |
| | | *Monochloro-substituted congeners* | | | | | | |
| 188 | 13.475 | 0.83 | 20.94 | 102.93 | 97.54 | 81.31 | 54.18 | 1.12 |
| 188 | 14.458 | 0.39 | 12.03 | 45.06 | 23.46 | 12.74 | 3.47 | 0.04 |
| 188 | 14.558 | 0.9/0.09 | 20.53 | 44.83 | 18.76 | 25.19 | 25.55 | 0.08/<br>**0.004** |
| | **Mono-CB total** ‰ **w/w** | **0.21** | | | | | | **0.06** |
| | | *Dichloro-substituted congeners* | | | | | | |
| 222 | 15.083 | 9.12 | 26.34 | 55.41 | 81.99 | 118.96 | 117.75 | 2.53 |
| 222 | 15.717 | 2.18 | 52.39 | 34.58 | 13.08 | 5.34 | 1.51 | 0.09 |
| 222 | 15.975 | 2.94 | 20.48 | 29.32 | 19.4 | 12.97 | 4.31 | 0.07 |
| 222 | 16.125 | 57.51/**5.57** | 139.98 | 93.9 | 4 1.59 | 17.61 | 4.02 | 1.06/<br>**0.05** |
| 222 | 16.608 | 1.36 | | | | | | 0.12 |
| 222 | | | 1.89 | 1.77 | 0.67 | | | |
| 222 | 17.083 | 1.32 | 49.83 | 12.54 | 2.8<br>5.18 | 0.31 | | |
| 222 | 17.217 | 33.08 | 25.26 | 9.85 | 1.12 | | 0.52 | 0.24 |
| | **Di-CB total** ‰ **w/w** | **10.28** | | | | | | **0.2** |
| | | *Trichloro-substituted congeners* | | | | | | |
| 256 | 16.608 | 4.59 | 6.99 | 7.06 | 5.99 | 4.9 | 1.83 | |
| 256 | 17.142 | 59.05 | 70.24 | 55.41 | 38.36 | 28.85 | 8.86 | 1.81 |
| 256 | 17.192 | 29.31 | 39.3 | 26.3 | 15.49 | 6.39 | 1.73 | |
| 256 | 17.383 | 4.64 | 6.33 | 3.21 | 1.25 | 0.78 | 0.12 | 0.13 |
| 256 | 17.592 | 45.67 | 57.93 | 32.79 | 13.25 | 5.87 | 1.38 | 0.89 |
| 256 | 17.817 | 2.66 | 3.8 | 1.4 | 0.15 | | | 0.04 |
| 256 | 17.892 | 3.23 | 11.99 | 3.65 | 0.69 | 0.56 | 0.25 | 0.11 |
| 256 | 18.000 | 9.04 | 11.18 | 5.1 | 1.4 | 0.68 | 0.15 | 0.17 |
| 256 | 18.058 | 4.76 | 7.98 | 2.83 | 0.56 | 0.35 | 0.12 | 0.13 |
| 256 | 18.208 | 61.09 | 86.52 | 29.65 | 5.29 | 2.74 | 2.24 | 1.8 |
| 256 | 18.250 | 238.21/<br>**23.06** | 159.34 | 26.95 | 15.48 | 5.61 | | 5.11/<br>**0.25** |
| 256 | 18.450 | 68.52 | 83.52 | 25.83 | 6.95 | 4.49 | 1.43 | 1.89 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 256 | 18.625 | 33.27 | 41.35 | 12.53 | 2.87 | 1.66 | 0.51 | 0.89 |
| 256 | 19.392 | 0.55 | 2.74 | 0.42 | 0.27 | | 0.07 | 0.1 |
| 256 | 19.575 | 47.13 | 23.37 | 4.39 | 0.79 | 1.08 | 0.32 | 0.94 |
| 256 | 19.659 | | | 0.15 | 0.16 | 0.62 | 0.3 | |
| 256 | 17.916 | | | | | | 0.98 | 0.14 |
| | **Tri-CB total ‰ w/w** | **59.23** | | | | | | **0.7** |
| | | *Tetrachloro-substituted congeners* | | | | | | |
| 290 | 18.463 | 3.99 | 5.07 | 4.62 | 2.69 | 2.51 | 0.8 | 0.07 |
| 290 | 18.568 | 1.89 | 2.24 | 1.53 | 0.52 | 0.43 | 0.08 | 0.03 |
| 290 | 18.730 | 4.42 | 4.92 | 2.24 | 0.43 | | 0.08 | 0.08 |
| 290 | 18.900 | 1.63 | 2.09 | 1.37 | 0.4 | | 0.04 | 0.02 |
| 290 | 18.993 | 18.03 | 19.79 | 11.4 | 4.29 | 2.00 | 0.41 | 0.42 |
| 290 | 19.097 | 19.28/ **1.87** | 19.82 | 9.45 | 2.82 | 1.31 | 0.32 | 0.46/ **0.023** |
| 290 | 19.172 | 24.4 | 23.79 | 9.28 | 2.11 | 1.12 | 0.31 | 0.68 |
| 290 | 19.465 | 15.46 | 16.84 | 7.53 | 1.83 | 1 | 0.26 | 0.37 |
| 290 | 19.549 | 10.42 | 9.43 | 3.15 | 0.77 | 0.55 | 0.11 | 0.26 |
| 290 | 19.733 | 10.61 | 12.54 | 2.85 | 1.39 | 0.31 | | 0.74 |
| 290 | 19.758 | 22.84 | 19.0 | 5.32 | 0.11 | 0.96 | 0.34 | |
| 290 | 19.946 | 3.81 | 3.8 | 1.25 | 0.11 | 0.15 | 0.04 | 0.09 |
| 290 | 20.067 | 1.79 | 1.83 | 0.35 | | | | |
| 290 | 20.200 | 4.78 | 3.59 | 0.82 | | | | 0.87 |
| 290 | 20.295 | 38.92 | 29.46 | 5.61 | 1.27 | 0.93 | 0.26 | 0.84 |
| 290 | 20.377 | 30.82 | 21.84 | 5.01 | 1.05 | 0.8 | 0.23 | |
| 290 | 20.471 | 39.43/ **3.82** | 22.62 | 4.61 | 1.13 | 0.8 | 0.19 | 1.12/ **0.055** |
| 290 | 20.675 | 1.3 | 0.6 | 0.05 | | | | |
| | | | 0.04 | | | | | |
| 290 | 20.887 | 31.55 | 19.38 | 3.86 | 0.73 | 0.66 | 0.19 | 0.87 |
| 290 | 22.008 | 3.93 | 1.07 | 0.16 | | | | |
| | **Tetra-CB total ‰ w/w** | **28.0** | | | | | | **0.34** |
| | | *Pentachloro-substituted congeners* | | | | | | |
| 324 | 20.450 | 0.29 | 0.29 | 0.15 | 0.02 | | | |
| 324 | 20.476 | 1.34 | 1.5 | 0.81 | | 0.06 | 0.02 | |
| 324 | 20.628 | 0.55 | 0.53 | 0.12 | | | | |
| 324 | 20.892 | 0.15 | 0.15 | 0.05 | | | | |
| 324 | 21.023 | 2.83/ **0.27** | 2.98 | 0.99 | 0.04 | 0.08 | 0.02 | 0.08/ **0.004** |
| 324 | 21.155 | 2.59 | 2.25 | 0.69 | | 0.05 | | |
| 324 | 21.574 | 0.83 | 0.82 | 0.21 | | | | |
| 324 | 21.706 | 1.4 | 1.07 | 0.08 | | | | |
| 324 | 21.824 | 1.26 | 0.65 | 0.03 | | | | |
| 324 | 21.964 | 2.6 | 1.77 | 0.29 | | 0.03 | | 0.08 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 324 | 22.267 | 0.33 | 0.16 | | | | | |
| 324 | 22.533 | 0.16 | | | | | | |
| 324 | 22.665 | 3.05/**.3** | 1.78 | 0.28 | | 0.02 | | **/0** |
| 324 | 23.429 | 1.57 | 0.45 | 0.04 | | | | |
| 324 | 22.692 | | | 0.3 | | | | 0.06 |
| 324 | 23.425 | 1.6 | 0.5 | | | | | 0.01 |
| | **Penta-CB total ‰ w/w** | **1.99** | | | | | | **0.011** |

<u>Note:</u> Retention time is expressed in minutes. Mass 154 corresponds to biphenyl, 188 to monochloro-substituted PCB congeners, 222 to dichloro-, 256 to trichloro-, 290 to tetrachloro-, and, finally, 324 to pentachloro-substituted.

**Table 7. Changes in the composition of the technological fluid *Trichlorodiphenyl* (*Arochlor* 1242 analogues) during the test (‰ w/w). Only most abundant congeners have been included.**

| | **Concentatrion, C'** | | **Relative rate, $V_{rel}$** | **Rate ratio** |
|---|---|---|---|---|
| **Congeners** | **0 min.** | **360 min.** | **$V_{rel}$ = C'0/C/360** | **$V_{rel}$/180.9** |
| biphenyl | 6.29 | 98.69 | | |
| mono-CB | 0.21 | 0.06 | 3.5 | 0.02 |
| 188/14.558 | 0.09 | 0.004 | 22.5 | |
| di-CB | 10.28 | 0.2 | 5.14 | 0.03 |
| 222/16.125 | 5.57 | 0.05 | 111.4 | |
| tri-CB | 59.23 | 0.7 | 84.6 | 0.47 |
| PCB 28/31 | 23.06 | 0.25 | 92.2 | |
| tetra-CB | 28.0 | 0.34 | 82.35 | 0.46 |
| PCB 52 | 1.87 | 0.023 | 81.3 | |
| 290/20.471 | 3.82 | 0.055 | 69.45 | |
| penta-CB | 1.99 | 0.011 | 180.9 | 1 |
| PCB 101 | 0.27 | 0.004 | 67.5 | 0.37 |
| PCB 118 | 0.3 | 0 | high | |

A first order equation well fits the biphenyl accumulation curve (see Fig. 1) as well as the disappearance of penta- and tetra-CBs (Figs. 2-4).

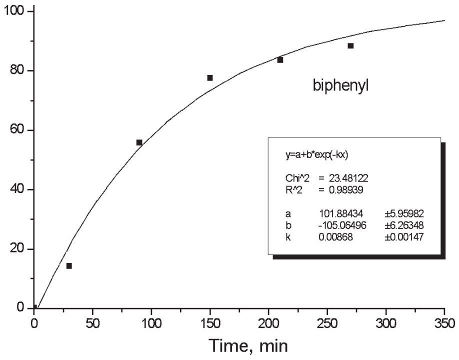

**Fig. 1. Biphenyl accumulation during HDC reaction.**

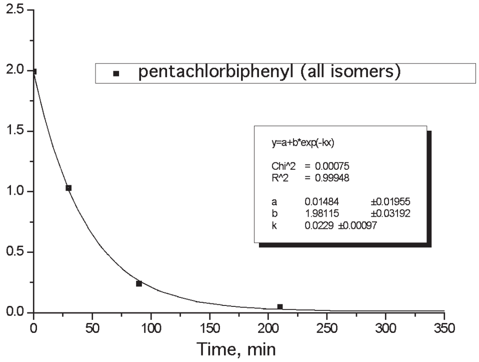

Fig. 2. Pentachlorobiphenyl consumption during HDC reaction.

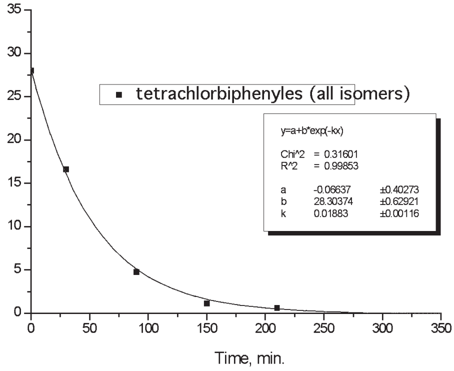

Fig. 3. Tetrachlorobiphenyl consumption during HDC reaction.

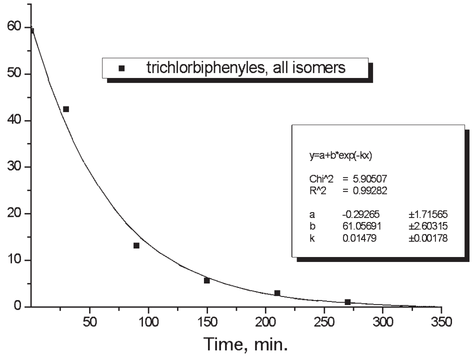

Fig. 4. Trichlorobiphenyl consumption during HDC reaction.

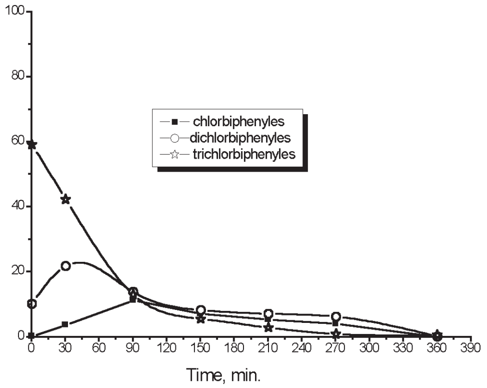

**Fig. 5. Changes in monochloro-, dichloro- and trichloro-substituted biphenyl concentrations.**

At the same time, mono- and di-CBs shape a characteristic “hump” on the kinetic curves (about 90 and 30 min, respectively). These data confirm a generic conclusion: the more chlorine atoms in the PCB molecule, the higher is their elimination rate under HDC and, evidently, under other destructive reactions related with the chlorine removal (Fig. 5).

A comparison of the PCB 101 (2,2’,4,5,5’-PeCB) and PCB 118 (2,3’,4,4’,5-PeCB) disappearance rates (Figures 6 and 7) evidences that the molecule’s capacity to assume a co-planar (flat) position may enhance molecule bonding to the heterogeneous catalyst.

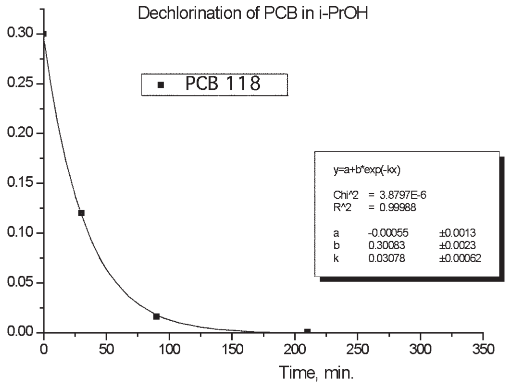

**Fig. 6. Determination of the HDC reaction rate constant for PCB 118.**

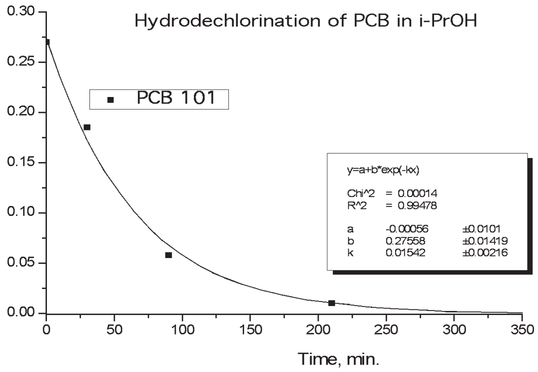

**Fig. 7. Determination of the disappearance rate constant for PCB 101.**

In the reported examples, PCB 118 (toxic, mono-*ortho*-substituted) shows a much higher reaction rate than di-*ortho*-substituted PCB 101. It is noteworthy that the latter molecule may assume a planar conformation. Such issues will be addressed in more detail in a separate research.

## CONCLUSIONS

- In relation to PCB-based commercial fluids used for electric technological (dielectric) applications, it was shown that their HDC carried out with a palladium catalyst leads to full chlorine elimination from PCB, yielding biphenyl. A 100%-conversion is achieved during periods varying from 0.5 to 1.5 h at room temperature.
- The reaction rate grows as the number of carbon atoms in the solvent decreases, when alcohols are used as solvents.
- HDC of *ortho*-substituted chlorobiphenyls in liquid-phase proceeds slower than HDC of PCBs containing chlorine atoms in other positions of the aromatic ring. As shown in previous researches, the same is true for gas-phase reactions.
- Kinetic parameters were obtained for individual chloro-BP groups. The reaction rate was found to be proportional to the number of chlorine atoms in the BP molecule. Due to that, a temporary mono- and dichloro-BP accumulation occurs in the reaction course.
- The formulation of Russian electric technological oils (for transformers and condensers) and their composition in congeners have been investigated. It has been established that the *Sovtol*-10 oils, in addition to PCB congeners, contains large amounts of toxic dioxins/furans, which make these oils highly hazardous for both environment and human health.
- As a general conclusion, the HDC method can serve as a basis to conceive new technical solutions for waste-minimizing, exploiting green chemistry principles for destruction of PCBs and other toxic chlorinated chemicals.

## REFERENCES

1 Chemical Goods. Handbook, vol. II, Moscow, Khimia, 1969, p. 350. Harmful Substances in Industry. Handbook, ed. by N.V. Lazarev and E.N. Levina, volume I, Organic Chemicals. Leningrad, Khimia, 1976, p. 309, 322.

2 Harmful Chemicals. Handbook, ed. by V.A. Filov and L.A. Tiunov. S.-Petersburg, Khimia, 1994, 688 p.

3 Polychlorinated Biphenyls. Supertoxicants of 21 Century. Inf. Bull. No. 5. VINITI, Moscow, 2000.

4 N.A. KLUYEV and E.S. BRODSKY. Identification of polychlorinated biphenyls in the environment and biota. In: Polychlorinated Biphenyls. Supertoxicants of 21st Century. Inf. Bull. No. 5. VINITI, Moscow, 2000.

5 Polychlorinated Biphenyls. Bull. No. 107, ed. by N.F. Izmerov, UNEP, CMP GKNT, Moscow, 1988.

6 S. YUFIT, E. GROSHEVA, J. ADIBI. An effort to inventory dioxin releases to air and dioxin levels in Russia's environment. Organohalogen Compounds 2001, 50, 401-406]

7 ELI Eco Logic International Inc.

8 C.A. MARQUES, M. SELVA, P. TUNDO. J. Chem. Soc., Perkin Trans. I (1993) 529. C.A. Marques, M. Selva, P. Tundo. Facile HDH with $H_2$ and Pd/C catalyst under multiphase conditions. 2. Selectivity and kinetics [JOC, 1994, 59, 3830-3837].

9 L.N. ZANAVESKIN, V.A. AVER'YANOV. Polychlorobiphenyls: problems of the pollution of the environment and technological neutralization methods. Russian Chemical Reviews, 1998, vol. 67, No. 8, p.713-724.

10 F.J. URBANO, J.M. MARINAS Hydrogenolysis of organohalogen compounds over palladium supported catalysts. J. Mol. Cat. A: Chemical 173 (2001) 329-345.

11 V.V. LUNIN, E.S. LOKTEVA. Russ. Chem. Bull. 45 (1996) 1519.

12 Y.UKISU, T. MIYADERA. J. Mol. Catal. A 125 (1997) 135. Y.Ukisu, S. Kameoka, T. Miyadera. Appl. Catal. B 18 (1998) 273.

13 CH. SCHÜTH, M. REINHARD. Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water. Applied Catalysis B: Environmental 18 (1998) 215-221.

14 GUO-BIN LIU, TAKEHITO TSUKINOKI, TADASHIGE KANDA, YOSHIHARU MITOMA, MASASHI TASHIRO. Organic reaction in water. Part 2. A new method for dechlorination of chlorobiphenyls using a Raney Ni-Al alloy in dilute aqueous alkaline solution. Tetrahedron Lett. 39 (1998) 5991-5994.

15 P. FORNI, L. PRATI, M. ROSSI. Catalytic dehydrohalogenation of polychlorinated biphenyls. Part II: Studies on a continuous process. Applied Catalysis B: Environmental 14 (1997) 49-53.

16 F. MURENA, E. SCHIOPPA, F. GIOIA. Catalytic hydrodechlorination of PCB dielectric oil. Environ. Sci. Technol. 2000, 34, 4382-4385. F. Murena, E. Schioppa. Kinetic analysis of catalytic hydrodechlorination process of polychlorinated biphenyls (PCBs). Applied Catalysis B: Environmental 27 (2000) 257-267.

17 R.B. LAPIERRE, L. GUCZI, W. L. KRANICH, A.H. WEISS. Hydrodechlorination of polychlorinated biphenyl. Journal of Catalysis 52, 230-238 (1978).

# CATALYTIC DECHLORINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN WATER UNDER SUBCRITICAL CONDITIONS

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A major present environmental problem is environmental pollution due to persistent organic pollutants (POPs). The most hazardous ones among them are the polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). Even minor doses of these xenobiotics ($1 \bullet 10^{-14}$ to $1 \bullet 10^{-9}$ g/g or g/ml) intensify functioning of hepatic monooxygenase system enzymes, thus causing a metabolic chaos. In fact this enzymatic system is responsible both for the detoxification of hundreds of substances entering the organism and for the synthesis of necessary molecules.

High and low resolution chromatography-mass-spectrometry techniques [1, 2] help to solve analytical problems associated with the identification and quantization of superecotoxicants. Major dioxin sources and polluted areas have been identified and categorized [3, 4]. The emissions of toxicants from each industrial sector are annually monitored in each developed country. This greatly contributes to the control of their environmental emission levels [3, 5]. However, the reclamation of contaminated sites still remains an issue to be addressed. In the case of dioxins, incineration – applied for the destruction of many hazardous chemicals – may produce even larger dioxin amounts [6, 7]. The dioxin toxicity specifics implicates that only 2,3,7,8-halogen-substituted congeners pose a risk, the rest being quite safe with respect to their concentrations. Hence, for detoxication, it is enough to remove one halogen atom from lateral positions of the heterocycle. At present days, intensive efforts are being made to identify microorganisms capable of breaking C-Cl bonds. A method using alkaline hydrolysis in subcritical conditions gives encouraging results and may appear useful in the treatment of fly-ashes from incinerators and other thermal processes [8, 9].

A more challenging issue is detoxication of soils. The half-life of dioxins in soils ranges from 10 to 20 years [3]. Dioxins are characterized by low effective solubility in water at normal temperatures: about 20 ng/l for the most soluble, 2,3,7,8-TCDD [10], and 2.3 pg/l for the least soluble, OCDD [3]. Considering such factor along with high sorption capacity of soils, it is clear that organic solvents are needed for extraction of dioxins and subsequent dechlorination. The use of these solvents makes the decontamination process unacceptable in terms of costs and environmental risks.

Lately, processes occurring in aqueous phase under subcritical conditions attracted interest of researchers from different countries. It has been reported that solubility of some xenobiotics, including dioxins, increases by several orders of magnitude when temperature is raised from 20 to 250°C [12, 13]. In such cases water may become a good solvent for extraction of these chemicals from soil. Then a photolytic or another dechlorination reaction may be used for detoxication [14]. Even more beneficial could be a combined extraction/ dechlorination process in subcritical conditions. The results of dechlorination of polychlorinated biphenyls (PCBs) supported on iron powder in an aqueous phase at 250-300°C was reported in our past studies [15]. We also showed that water in subcritical conditions could be used for the extraction of PCDD/PCDF from soils [13], i.e. desorbing dioxins from soil particles and transferring them to the surface of the reducing agent. In particular, if compared to the value at room temperature, at 250ºC solubility of octachlorodibenzo-p-dioxin (OCDD) increases by a factor $2{\cdot}10^6$. We reported in our past investigations that metallic iron was able to start stepwise dechlorination of PCDD [16]. At the same time, while examining the dechlorination process of OCDD (a 2,3,7,8-substituted congener with lowest toxicity), we found that the most toxic dioxin, 2,3,7,8-TCDD, was present in the system and contributed to a higher total toxicity value (I-TEQ). Apparently, the concentration of 2,3,7,8-TCDD was due to a sort of "equilibrium", rather than accumulation. This phenomenon most probably originates from an activation energy rise corresponding to the decrease of the chlorination degree. A similar occurrence was described for PCB dechlorination under analogous conditions [15, 17]. Basing on these issues, in order to enhance the reaction efficiency and overcome the energetic barrier it seemed appropriate to employ catalysts.

Raney-nickel (Ni-Re) and Aliquat 336® were used in this research, since they proved to be highly efficient in the phase-transfer hydrodechlorination reactions [18].

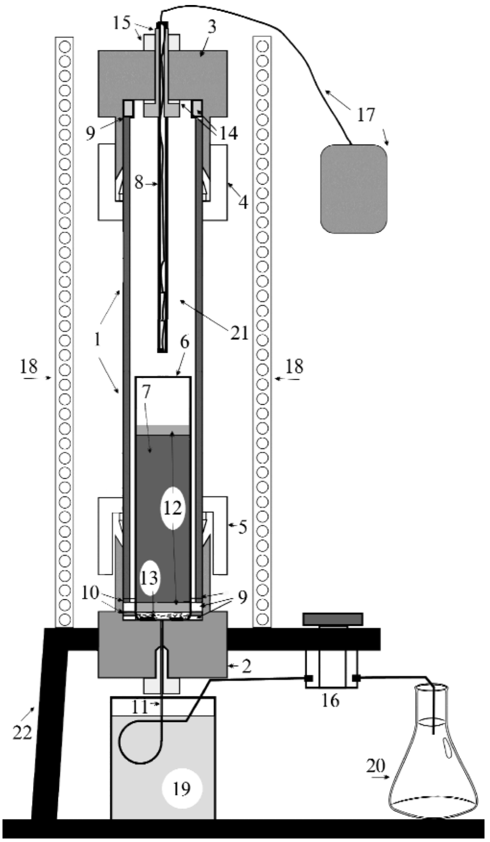
## EXPERIMENTAL

Silica gel (grain size 0.063 - 0.200 mm), iron powder (grain size ≈ 0.1 mm), Aliquat 336 solution in ethanol (10% v/v) and Raney-nickel were used in the experiments. All solvents and solids employed were tested for the presence of PCDD/PCDF. OCDD and OCDF were synthesized by perchlorination from unsubstituted homologues [19] and tested against the presence of less chlorinated congeners – PCDD and PCDF – by GC-HRMS (gas chromatography combined with high resolution mass-spectrometry).

Silica gel served as a soil analog. Dioxins were supported on the silica gel according to the following procedure. A portion of silica gel (5 g) was placed in a 200 - 250 ml beaker, whereto acetone was added in order to moisten 70-80% of the surface. After that, an OCDD-OCDF mixture was placed into the beaker and acetone was added until the whole silica gel was moistened. Next, the beaker was kept in a ultrasonic bath for 30 min. Acetone was evaporated in a chemical hood during 3 days with periodic silica gel stirring with a glass stick. A new portion was prepared for each test. Iron powder (0.5 g) was added to the pretreated silica gel prior to each test. Raney-Ni was introduced as a water suspension (total mass 0.25 g); Aliquat 336 was used as a 10% solution in ethanol (1 ml). Samples were thoroughly stirred after the addition of each ingredient. The prepared mixture was housed inside the extractor's sample holder. To avoid losses due to adhering of silica gel particles onto the beaker walls, the latter were cleaned with a quartz fiber wad, which was placed in the holder as well.

For the experiments a new plant for subcritical extraction under equilibrium pressure was realized (Fig. 1). Its advantage over the old plant was the absolute containment, now achieved through increasing the contact area of screw nuts (4 and 5) and the extractor shell (1), without changing the reaction chamber dimensions.

The experiments were carried out according to the following procedure. A cartridge with a sample (6) was installed in the lower cover (2) and the column was fixed (1). Next, the system was filled with water (total volume about 90 cm$^3$), the valve (16) being open. Then the latter was closed and the upper cover tightened up. The system was heated up to 250°C for 25-30 min; a temperature of 250-260°C was maintained for 60 min. After valve (16) re-opening, the water fraction was let out at the rate of about 20 ml/min. A mixture of isotope-labeled internal standards was added to the aqueous phase and extraction was performed by three dichloromethane portions (50, 25 and 25 ml). Extraction of residual PCDD and PCDF was conducted by toluene at 160-170ºC. The organic extracts were joined together and treated in a sandwich column, a charcoal column and, finally, a column with alumina as described in [20]. The analysis was made using the high resolution chromatography-mass-spectrometry system Finnigan MAT 95XL. Identification of 2,3,7,8-substituted congeners was performed by retention times; their quantization was achieved through correlation of the areas of the identified congener's peaks and of the corresponding peak of the standard. The other congeners were determined as groups without individual identification.



All the parts of the plant contacting with the solvent, except for the separators, are made of stainless steel.

1 - column, length 25 cm,
internal diameter 21 mm
2 - lower cover
3 - upper cover
4 - upper screw nut
5 - lower screw nut
6 - sample holder
7 - sample
8 - thermocouple tube
9 - Teflon separators
10 - steel rings
11 - cooled capillary
12 - quartz fiber filters
13 - mesh
14 - aluminum separators
15 - thermocouple tube fixing
and sealing gadget
16 - valve
17 - thermocouple
18 - heater
19 - beaker with water
20 - receiving vessel
21 - solvent
22 - support

**Fig. 1. A plant for subcritical extraction under equilibrium pressure.**

## RESULTS AND DISCUSSION

The results of this research are summarized in Table 1 and in Figs. 2-4. As found out in previous studies, when PCDD and PCDF supported on silica gel are treated with water under subcritical conditions, no significant changes in the amounts or congener composition are found. Therefore, it is possible to assume that the observed changes result from the influence of the introduced reagents.

The experimental results demonstrate that stepwise dechlorination, which mainly produces non-toxic congeners, occurs in both events: when either pure iron or a catalyst is added to the system (Fig. 3). Raney-nickel and Aliquat 336 additives speed-up dechlorination of starting compounds and reduce the amount of low-chlorinated 2,3,7,8-substituted congeners PCDD/PCDF in the system, thereby leading to a total toxicity decline (Fig. 3). The profile obtained for the congeners allows assuming that catalytic additives do not involve changes of the reaction type, because in water, under subcritical conditions, alternative processes occur in parallel. They may be characterized as "hydrothermal destruction". Its mechanism has not been investigated so far; presumably, it could be either hydrolysis or oxidation. The only fact that has been clarified is that the destruction is caused by substances available in some soils and bottom sediments and that the process does not generate less chlorinated congeners [21].

In all the tested systems, dechlorination predominantly yields congeners that do not have four lateral atoms, i.e. a specific dioxin toxicity loss is typical for the reaction (Figs. 3-4). The single exception is dechlorination of OCDF where products from apical substitution initially prevail.

The collected data also confirm the assumption that the dechlorination reaction rate decreases with a chlorination degree decline. For example, if Raney-Ni and Aliquat 336 were simultaneously used, actual full disappearance of starting OCDD and OCDF was observed. This happened even if dechlorination products - including most toxic 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF - were present in the system. This feature distinguishes such process from the dioxin degradation one occurring in the environment, where the highly-chlorinated congeners are the most persistent. In particular, stepwise dechlorination proceeds under the photolysis, yet no congeners with chlorination degrees below six are normally detected [22]. On the other hand, in nature reductive dechlorination may explain an unusual congener profile in a few samples. Recent researches have revealed that sometimes PCDD is present in sites located far away from its emission sources. Moreover, no PCDF were found in those samples, this is extrinsic for all known dioxin sources [23, 24]. Presumably, one of the contamination sources for these samples is likely to be the OCDD photosynthesis from pentachlorophenol or its intermediates in the environment [25]. Low-chlorinated congeners cannot be generated by this mechanism; however, it is possible to assume that they are the products of a reductive dechlorination occurring in soils.

| Experiment conditions<br>Congener | Original mixture | After subcritical treatment in the presence of: | | |
|---|---|---|---|---|
| | | Iron | Iron and Raney-nickel | Iron, Raney-nickel and Aliquat 336 |
| 2,3,7,8-TCDD | 57.3 | 18 | 7.4 | 0.8 |
| 1,2,3,7,8-PeCDD | < d.l. | 209 | 71.7 | 7.7 |
| 1,2,3,4,7,8-HxCDD | < d.l. | < d.l. | 34.0 | 0 |
| 1,2,3,6,7,8-HxCDD | < d.l. | < d.l. | 34.0 | 8.5 |
| 1,2,3,7,8,9-HxCDD | < d.l. | 173 | 64 | 4.5 |
| 1,2,3,4,6,7,8-HpCDD | < d.l. | 153 | 239 | < d.l. |
| OCDD | 14,681 | 2,613 | 739 | 110 |
| 2,3,7,8-TCDF | < d.l. | 536 | 11.8 | 2.2 |
| 1,2,3,7,8-PeCDF | < d.l. | 128 | 10.4 | 0 |
| 2,3,4,7,8-PeCDF | < d.l. | 524 | 29,2 | 9.0 |
| 1,2,3,4,7,8-HxCDF | 190 | 195 | 106 | < d.l. |
| 1,2,3,6,7,8-HxCDF | < d.l. | 156 | 127 | 5.1 |
| 1,2,3,7,8,9-HxCDF | < d.l. | 396 | 159 | 4.8 |
| 2,3,4,6,7,8-HxCDF | < d.l. | 11 | 362 | < d.l. |
| 1,2,3,4,6,7,8-HpCDF | 358 | 1,014 | 782 | 10.0 |
| 1,2,3,4,7,8,9-HpCDF | 59.8 | 26 | 294 | 5.3 |
| OCDF | 79,487 | 6,849 | 1,759 | < d.l. |
| Other TCDD | < d.l. | 621 | 196 | 32.5 |
| Other PeCDD | < d.l. | 2,094 | 279 | 22.9 |
| Other HxCDD | < d.l. | 1,881 | 339 | 62.8 |
| Other HpCDD | < d.l. | 236 | 253 | 12.3 |
| Other TCDF | < d.l. | 13,746 | 504 | 81.8 |
| Other PeCDF | < d.l. | 6,985 | 1,076 | 148 |
| Other HxCDF | 1,708 | 2,018 | 696 | 111 |
| Other HpCDF | 530 | 384 | 409 | < d.l. |
| **I-TEQ** | **175** | **559** | **164** | **11.9** |
| **WHO-TEQ** | **89.9** | **655** | **198** | **15,6** |

***d.l.**: detection limit, 0.5 - 5 pg approx.*

**Table 1. Results of OCDD and OCDF dechlorination in aqueous phase at 250-260∞C and equilibrium pressure.**

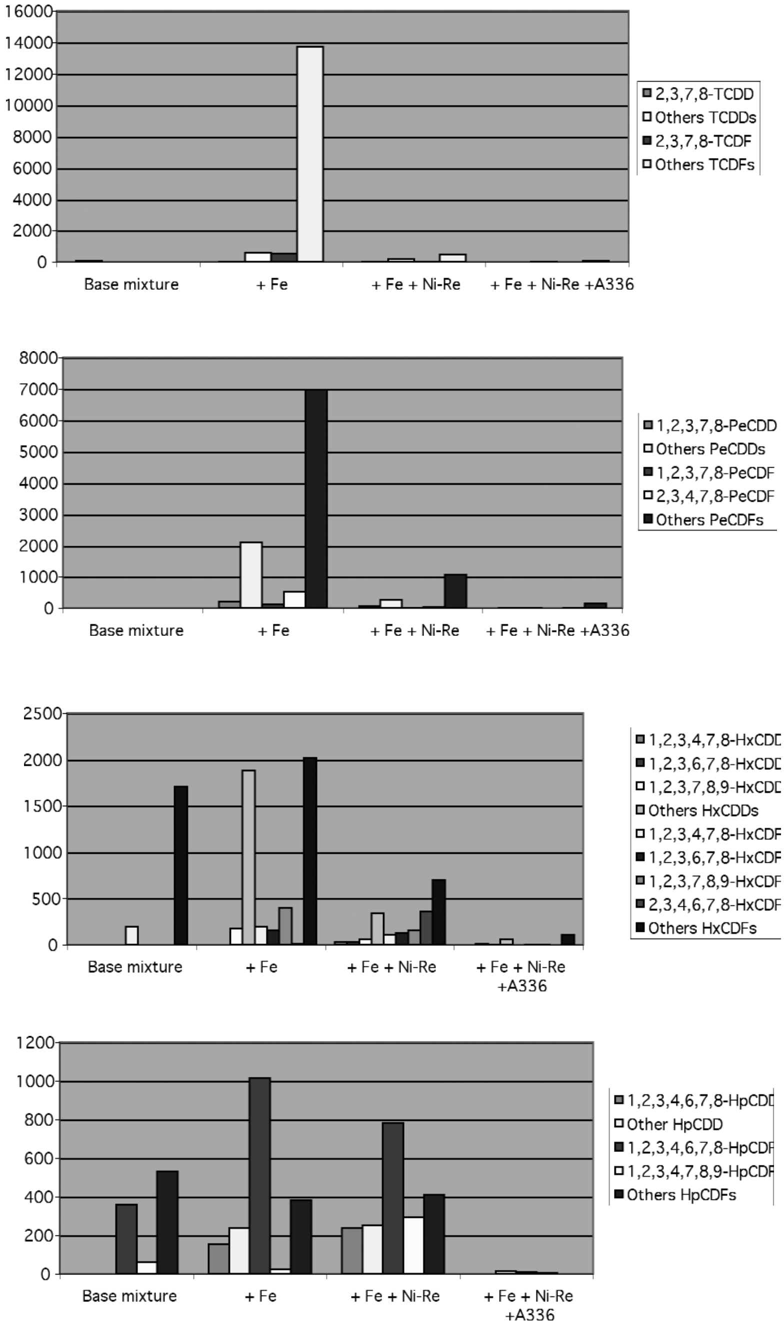


**Fig.2. Dependence of the PCDD/PCDF content on the reaction mixture composition, under reductive dechlorination of OCDD and OCDF.**

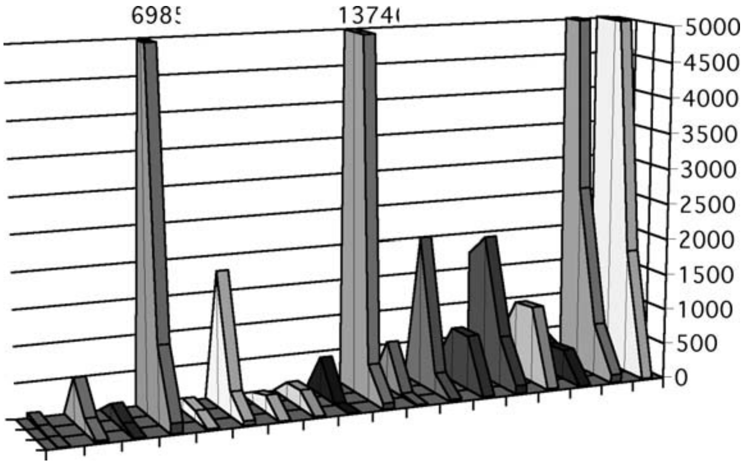


**Fig. 3. Changes in the amount (pg) of 2,3,7,8-substituted congeners and the totality of other PCDD/PCDF congeners, during reductive dechlorination carried out in a subcritical water phase.**

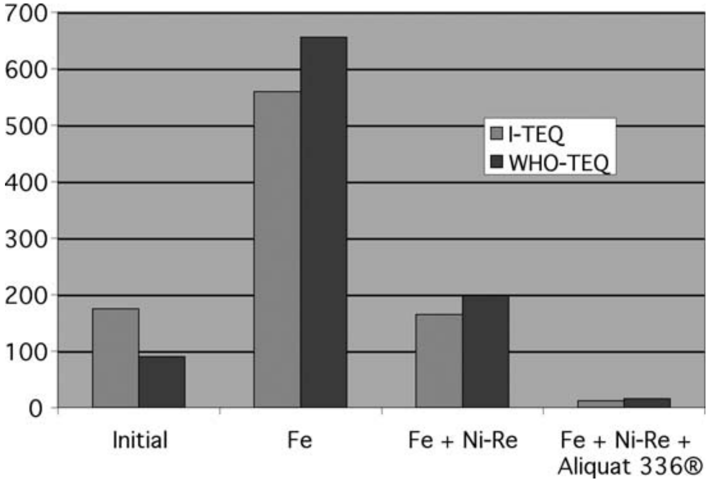


**Fig. 4. Change of the total toxicity (I-TEQ and WHO-TEQ), during dechlorination of OCDD and OCDF carried out in subcritical water.**

## REFERENCES

1 Kluyev N.A. (1996) Control of superecotoxicants in the environment and sources of their emergence. *JAKh* **51**, 2, 163-172.

2 Maistrenko V.N., Khamitov R.Z. and Budnikov G.K. (1996) *Environmental-Analytical Monitoring of Superecotoxicants*. M.: Khimia, 319 p.

*3* *Toxicological profile for chlorinated dibenzo-p-dioxins* (1997), Research Triangle Institute, 600 p.

4 Harrad S.J. and K.C. Jones (1992) A source inventory and budget for chlorinated dioxins and furans in the United Kingdom environment. *The Science of the Total Environment*, **126**, 89-107.

5 Rappe C. (1996) Sources and environment concentration of dioxin and related compounds. *Pure & Appl. Chem.*, **68(9)** 1781-1789.

6 Tanaka M., Watanabe I., Hiraoka M., Takizawa Y., Masuda Y., Takeshita R. and Yagome K. (1989). Formation and decomposition of dioxins and related compounds in fluidized bed incinerators. *Chemosphere.* **18 (1-6),** 321-328.

7 Tuppurainen K., Halogen I., Ruokojärvi P., Tarhanen J. and Rauskanen J. (1998) Formation of PCDD and PCDF in municipal waste incinerator and its inhibition mechanisms: a review. *Chemosphere.* **36, N.7,** 1493-1511.

8 Gräbel H.-P. and Hagenmaier H. (1998) Hydrothermal decomposition of PCDD/F. *Organohalogen Compounds.* **36,** 21-26.

9 Windal I., Hawthorne S. and Pauw E. De. (1999) Subcritical water degradation of dioxin. *Organohalogen Compounds.* **40,** 591-594.

10 Marple L., Brunck R. and Throop L., (1986) Water solubility of 2,3,7,8 Tetrachlorodibenzo-p-dioxin. *Environ. Sci. Technol.* **20**, 180-182.

11 McCrady and Maggard (1993) *Environ. Sci. Technol.* **27,** 343-350.

12 Yang Yu, Berlghazi M., Lagadec A., Miller D. J. and Hawthorne S. B. (1998) Elution of organic solutes from different polarity sorbents using subcritical water. *J. Chromatogr. A.* **810**, 149-159.

13 Soyfer V.S., Shelepchikov A.A., Kluyev N.A. and Rudenko B.A. (1999) Water in subcritical condition – an effective solvent for the extraction of dioxins from soils. *Organohalogen Compounds.* **41,** 425-429.

14 Choudhry G.G. and Webster G.R.B. (1985) Environmental photochemistry of PCDDs Part 1. Kinetics and quantum yields of the photodegradation of 1,2,3,4,7 Penta and 1,2,3,4,7,8 Hexachlorodibenzo-p-dioxin in aqueous acetonitrile. *Chemosphere*. **14 (1)**, 9-26.

15 Yak H.K., Wenclawiak B.W., Cheng I.F., Doyle J.G., Wai C.M. (1999) Reductive dechlorination of polychlorinated biphenyls by zerovalent iron in subcritical water. *Environ. Sci. Technol.* **33,** 1307-1310.

16 Kluyev N., Sheleptchikov A., Brodsky E., Soyfer V., Zhilnikov V. (2002) Reductive dechlorination of polychlorinated dibenzo-p-dioxins by zerovalent iron in subcritical water. Chemosphere **46**(9-10), 1293-1296.

17 Yak H.K., Lang Q., Wai C.M. (2000) Relative Resistance of Positional Isomers of Polychlorinated Biphenyls toward Reductive Dechlorination by Zerovalent Iron in Subcritical Water. Environ. Sci. Technol. **34**(13), 2792-2798.

18 Zinovyev S., Shinkova N., Tundo P. (2002) Multiphase Catalytic Hydrodechlorination of Polychlorinated Substrates over Raney-Nickel, Organohalogen Compounds**,** Summary and Supplements, 75-77.

19 Kluyev N.A., Feshin D.B., Brodsky E.S., Kalinkevich G.A., Soyfer V.S. (2003) Screening method of PCBs detection in environment by perchlorination reaction. Fresenius Environ. Bull. **12(2)** 148-151.

20 Cheleptchikov A.A., Kluyev N.A., Soyfer V.S., Feshin D.B., Brodsky E.S. (2002) Optimized manual sample preparation method for dioxin analysis. Organohalogen Compounds **55**, 81-84.

21 Kluyev N.A., Cheleptchikov A.A., Soyfer V.S., Brodskij E.S., Rudenko B.A. (2001) Subcritical Water Remediation Of PCDD/PCDF Contaminated Soil and Sediment Organohalogen Compounds 54, 153-156.

22 Vollmuth S., Zajc A., Niessner R. Formation of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans during the Photolysis of Pentachlorophenol-Containing Water. Environ. Sci. Technol. **28(6)**, 1145-1149.

23 Ferrario J.B., Byrne C., Cleverly D.H. (2000) 2,3,7,8-Dibenzo-p-dioxins in Mined Clay Products from the United States: Evidence for Possible Natural Origin. Environ. Sci. Technol. **34(21)**, 4524-4532.

24 Gaus C., Brunskill G.J., Connell D.W., Prange J., Müller J.F., Päpke O., Weber R. (2002) Transformation Processes, Pathways, and Possible Sources of Distinctive Polychlorinated Dibenzo-p-dioxin Signatures in Sink Environments. Environ. Sci. Technol. **36(16)**, 3542-3549.

25 Baker J.I., Hites R.A. (2000) Is Combustion the Major Source of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans to the Environment? A Mass Balance Investigation. Environ. Sci. Technol. **34(14)**, 2879-2886.

# HYDROGENOLYSIS OF CHLOROBENZENE AND HEXACHLOROBENZENE ON BIMETALLIC CATALYSTS

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Catalytic hydrodehalogenation (hydrogenolysis) has been recognized as the most universal and promising method for recycling and neutralization of halogenated organic wastes. It allows transformation of environmentally hazardous chemicals to valuable products without release of toxicants [1]. However, presently, the extent of catalytic hydrogenolysis applications is constrained due to the problem of designing sufficiently active and stable catalysts without generating hydrogen chloride, a corrosive by-product. Literature reported that an increased stability of heterogeneous catalyst in liquid-phase hydrodechlorination is achievable through the use of phase transfer agents (PTA) [2, 3] and alkali metal or ammonia additives [4]. The present research focused on the development of high performance catalytic systems. It included synthesis and analysis of bimetallic supported catalysts (mainly Pt, Co- and Fe-promoted palladium) in the hydrodechlorination reaction of chlorobenzene and hexachlorobenzene in the presence of phase transfer catalysts (PTC).

## EXPERIMENTAL

### PREPARATION OF CATALYSTS

Supported bimetallic Pd-Pt catalysts were prepared by impregnation from solutions of the starting components. First, solutions of both components were prepared. After preparation of the support, the catalytic system was dried at 130-150°C for five hours. *Sibunit* was employed as carrier: d = 0.1 mm; $S_{sp} = 370\ m^2/g$ (by BET); $V_{pore} = 0.4\ cm^3/g$; $V_{micropore} = 0.15\ cm^3/g$; mean pore size = 40 Å. The catalysts were reduced by sodium tetrahydroborate in a water-ethanol solution at a ratio $M:NaBH_4 = 1:3$ both at room temperature and at 250°C.

#### Analysis of catalysts

The catalysts were studied using methods of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPES) and X-ray diffraction (XRD).

Electron microphotographs were made with a transmission electron microscope TEM – 2010 at accelerating voltage 200 kV and resonance 0.14 nm. For their preparation, the samples were first pre-dispersed in alcohol. Then a drop of the suspension was placed on perforated carbon supports fixed on sample holders with copper grids.

The XPES analysis was conducted on an electron spectrometer VG ESCALAB manufactured by *VG Scientific* (UK). Electron emission was induced by soft x-ray radiation $AlK_\alpha$ so that the average free path of the electron λ was 20-30 Å, depending on the line analyzed. Thus the analyzed thickness of the sample surface was around 3λ, i.e. 60-90 Å.

The samples were fixed on a holder with a conducting vacuum-stable double scotch tape. Prior to registering, the samples were put under vacuum in the pretreatment chamber at about $P = 10^{-7}$ mbar. After that, samples were placed in the analyzer chamber where vacuum did not exceed $10^{-9}$ mbar. Main background gases were CO, $CO_2$, and $H_2O$.

Line identification and XPE spectra calibration were performed according to the procedures described in [5, 6] using the NIST X–Ray Photoelectron Spectroscopy Database. A quantitative analysis of the chemical composition of the analyzed layer was based on the ratio of the component core level intensities, with regard to empiric factors of atomic sensitivity [5].

Diffractograms were realized with a diffractometer URD – 6 (radiation $CuK_\alpha$ λ = 1,5418Å) by point-wise scanning with a step 0.05º and in-point accumulation time 10 s. The scanning angle varied from $10^{\circ}$ to $90^{\circ}$, 2θ degr. crystal phase identification was assisted by PCPDF and ICSD databases.

The lattice parameters were measured by peak positions. The Pd–Pt lattice parameters were defined by the position of the most intensive maximum 111. The error in this case was ± 0.005 Å.

The coherent scattering region (CSR) was measured by the half-width of the peaks. The size of CSR for the Pd-Pt alloy was determined on the basis of Sherrer formula by the half-width of the diffraction peak 111.

## Experimental conditions

### Gas-phase hydrodechlorination of tetrachloromethane

A weight portion of the pre-reduced catalyst (by $NaBH_4$) was placed in a flow gas-phase reactor, dried in a nitrogen flow for 20 minutes and additionally activated in a hydrogen flow at 250°C for 1 h; the catalyst volume was 3 ml. Experimental conditions: atmospheric pressure, temperature 250°C, and hydrogen feed rate 30 ml/min.

### Hydrodechlorination of chlorobenzene

A weight portion of the catalysts was calculated with regard to the Me:C-Cl bonds in molecular ratio (1:1000). Sodium boron hydride was dissolved in 4 ml water (on the basis of ratio $Me:NaBH_4 = 1:3$) and put into the reactor where the catalyst had been placed. The reduced catalyst was filtered and then washed with water. The phase transfer agent ($(CH_3)_4N^+Cl^-$) and 4 ml of 50% KOH were then added to the catalyst; KOH is needed for neutralization of HCl formed during the reaction. The catalyst was activated in a hydrogen flow for 60 minutes, constantly stirred, in a hydrogen atmosphere at room temperature and pressure. Further on, chlorobenzene-undecane solution was added to the system in 11 ml of organic phase, which consisted of 7 ml toluene and 4 ml isopropanol. Undecane was used as an internal standard.

The hydrodechlorination reaction of chlorobenzene was conducted in a glass thermostatic reactor fitted with an internal magnetic stirrer (stirring rate 1200 r/min). Reaction conditions: constant hydrogen pressure, 1 atm., and constant temperature, 55°C.

### Hydrodechlorination of hexachlorobenzene

A weight portion of the catalysts was calculated with regard to the Me:C-Cl bonds in molecular ratio. Sodium boron hydride was dissolved in 4 ml water (on the basis of ratio $Me:NaBH_4 = 1:3$)

and put into the reactor where the catalyst had been placed. The reduced catalyst was filtered and then washed with water. The PTA ($(CH_3)_4N^+Cl^-$) was added and then 6 ml of 50% KOH for neutralization of HCl as above. The catalyst was activated in a hydrogen flow during 60 minutes of constant stirring, in a hydrogen atmosphere at room temperature and pressure. Further on, chlorobenzene-undecane solution was added to the system in 17 ml of organic phase, consisting of 11 ml toluene and 6 ml isopropanol. Undecane was used as an internal standard.

The reaction products were analyzed on a gas-chromatograph Tsvet 500M fitted with a flame-ionization detector. The gas-carrier was Ar, the temperature ranged from 50 to 250°C, the column length was 3 m and its diameter 2.5 mm, it was filled with 5% SE-30 supported on Chromaton N-AW.

*Evaluation of catalyst activity*

The total activity of metals in hydrodechlorination of chlorobenzene is

$$A_1 = \frac{C^0_{CB} \cdot X_B}{\nu_{Me} \cdot \Delta t}$$

The total activity of metals in hydrodechlorination of hexachlorobenzene is

$$A_1 = \frac{6 \cdot C^0_{HCB} \cdot X_B}{\nu_{Me} \cdot \Delta t}$$

where

$C^0_{CB}$ - starting chlorobenzene concentration, mol/l;

$C^0_{HCB}$ - starting hexachlorobenzene concentration, mol/l;

$X_B$ - portion of benzene formed (a conversion level);

$\nu_{Me}$ - metal concentration in the system, g-atom Me/l;

$\Delta t$ - time, min.

## RESULTS AND DISCUSSION

### Catalytic properties

*Liquid-phase hydrodechlorination of chlorobenzene and hexachlorobenzene*

The supported bimetallic catalysts were studied in relation to the liquid-phase hydrodechlorination reaction of chlorobenzene. Table 1 summarizes the catalytic activity data for the tested bimetallic and monometallic catalysts, during the hydrogenolysis reaction. The latter was performed using active components in varying proportions and compositions.

**Table 1. Dependence of the activity (mol/g atom of Me*min) of supported bimetallic catalysts from the catalyst composition in HDC reactions of chlorobenzene.**

| No. | Catalyst | Δt, min | Me:(C - Cl) | $A_1$, [mol/min*g-atom Me] |
|---|---|---|---|---|
| 1 | 1%Pd/C | 80 | 1:1000 | 3.5 |
| 2 | 1%$Pd_{90}Pt_{10}$/C | 80 | 1:1000 | 6.3 |
| 3 | 1%$Pd_{85}Pt_{15}$/C | 80 | 1:1000 | 5.2 |
| 4 | 1%$Pd_{80}Pt_{20}$/C | 80 | 1:1000 | 5.4 |
| 5 | 1%$Pd_{65}Pt_{35}$/C | 80 | 1:1000 | 4.0 |
| 6 | 1%$Pd_{50}Pt_{50}$/C | 80 | 1:1000 | 3.4 |
| 7 | 1%Pt/C | 80 | 1:1000 | 0 |
| 8 | 1%$Pd_{50}Co_{50}$/C | 80 | 1:100 | 1.0 |
| 9 | 1%$Pd_{20}Co_{80}$/C | 80 | 1:100 | 0.9 |
| 10 | 1%$Pd_{10}Co_{90}$/C | 80 | 1:100 | 0.5 |
| 11 | 1%Pd/C(T) | 60 | 1:1000 | 5.5 |
| 12 | 1%$Pd_{90}Pt_{10}$/C(T) | 60 | 1:1000 | 10.4 |
| 13 | 1%$Pd_{85}Pt_{15}$/C(T) | 60 | 1:1000 | 6.1 |
| 14 | 1%$Pd_{80}Pt_{20}$/C(T) | 60 | 1:1000 | 6.9 |
| 15 | 1%$Pd_{65}Pt_{35}$/C(T) | 60 | 1:1000 | 6.7 |
| 16 | 1%$Pd_{50}Pt_{50}$/C(T) | 60 | 1:1000 | 5.0 |

The data of Tab. 4 show that supported Pd-Pt catalysts exhibit higher activity in hydrochlorination of chlorobenzene than Pd-Co catalysts, even at lower 'supported metal-substrate' proportions. For instance, with equal amounts of supported palladium, 1% $Pd_{50}Pt_{50}$/C and 1% $Pd_{50}Co_{50}$/C, activities of the catalysts are 3.4 mol/min*g-atom Me and 1.0 mol/min*g-atom Me at metal-substrate ratios of 1:1000 and 1:100, respectively.

Some regularities were also revealed, which typically indicate the dependence of the catalyst activity both on the composition of the active component and on the preparation technique. The catalysts containing one sole pure metal, such as cobalt and platinum, were absolutely inactive under the test conditions. The activity of the Pd-Pt catalysts was visible after reduction both at room temperature and at 250°C and exhibited a non-additive activity increase when Pt was introduced (Table 1, No. 2, 3, 4, 12, 13, and 14). All samples reduced at 250°C were more active than corresponding samples reduced at the room temperature (Fig. 1). For example, activity of 1% $Pd_{90}Pt_{10}$/C increased from 6.3 to 10.4 mol/min*g-atom Me, depending on the temperature range of reduction.

Fig. 1 shows the activity values for supported bimetallic Pd-Pt catalysts varying with the palladium percentage and preparation techniques.

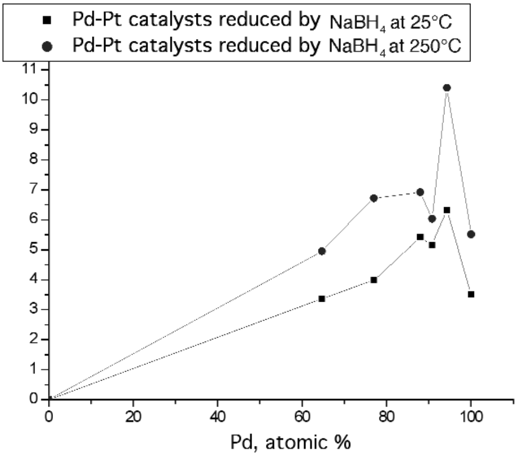

**Fig. 1. Activity [mol/min*g-atom Me] of supported catalysts in hydrodechlorination of chlorobenzene with different palladium percentages.**

A comparison of the data on activity of Pd-Pt catalysts in relation to their reduction temperature evidences that higher activity is showed by the samples reduced at superior temperatures. Notwithstanding their reduction temperature, a non-additive increase of activity of catalysts is observed when Pt is added to the active component (5.7-23 atomic %).

Pd-based bimetallic catalysts containing Pt, Fe, Ni or Co as second metal were tested in the reaction of liquid-phase hydrodechlorination of a more stable organochlorine compound: hexachlorobenzene. Table 2 lists data about the performance of the tested bimetallic and monometallic catalysts during the hydrogenolysis. The reaction was performed using varying proportions and compositions of the active component.

For all tested catalysts the activity also depends on the composition and proportions of the active components. Supported Pd-Pt catalysts exhibit higher activity in HDC of hexachlorobenzene at lower “supported metal-substrate” ratios (Table 2). Activity of the Pd-Pt systems varies from 18 to 44, when the ratio between the supported metal and the number of Cl atoms in the substrate is 1:500. In PD-Fe systems, when such ratio is 1:50, activity of the catalysts ranges from 1 to 2 (Table 2). With the same ratio (1:50), activity of the Pd-Ni catalysts is 0.04 - 0.5 and that of the Pd-Co catalysts varies from 1.1 to 1.7. We can note that the catalysts containing pure metals, such as cobalt and platinum, are absolutely inactive under the tested conditions. The tabulated data allow arranging activities of supported bimetallic catalysts in HDC reactions of hexachlorobenzene in the following sequence: Pd-Pt > Pd-Fe ≈ Pd-Co > Pd-Ni.

**Table 2. Dependence of the activity (mol/g atom Me*min) of supported bimetallic catalysts from the catalyst composition in HDC reactions of hexachlorobenzene.**

| No. | Catalyst | Δt, min | $X_B$ | Me:(C – Cl) | $A_1$, [mol/min*g-atom Me] |
|---|---|---|---|---|---|
| 1 | 1%Pd/C | 90 | 0.38 | 1:500 | 19.8 |
| 2 | 1%$Pd_{95}Pt_5$/C | 90 | 0.95 | 1:500 | 35.5 |
| 3 | 1%$Pd_{90}Pt_{10}$/C | 90 | 1.0 | 1:500 | 43.6 |
| 4 | 1%$Pd_{85}Pt_{15}$/C | 90 | 0.92 | 1:500 | 36.2 |
| 5 | 1%$Pd_{50}Pt_{50}$/C | 90 | 0.916 | 1:500 | 26.8 |
| 6 | 1%$Pd_{10}Pt_{90}$/C | 90 | 0.466 | 1:500 | 18.1 |
| 7 | 1%Pt/C | 90 | 0 | 1:500 | 0 |
| 8 | 3%$Pd_{20}Fe_{80}$/C | 120 | 0.855 | 1:50 | 2.2 |
| 9 | 3%$Pd_{10}Fe_{90}$/C | 120 | 0.609 | 1:50 | 0.98 |
| 10 | 3%$Pd_5Fe_{95}$/C | 120 | 0.263 | 1:50 | 1.09 |
| 11 | 3%$Pd_{20}Ni_{80}$/C | 120 | 0.495 | 1:50 | 0.55 |
| 12 | 3%$Pd_{10}Ni_{90}$/C | 120 | 0.158 | 1:50 | 0.04 |
| 13 | 3%$Pd_5Ni_{95}$/C | 120 | 0.109 | 1:50 | 0.21 |
| 14 | 3%$Pd_{20}Co_{80}$/C | 120 | 1.0 | 1:50 | 1.71 |
| 15 | 3%$Pd_{10}Co_{90}$/C | 120 | 0.966 | 1:50 | 1.79 |
| 16 | 3%$Pd_5Co_{95}$/C | 120 | 0.393 | 1:50 | 1.11 |
| 17 | 3%Co/C | 120 | 0 | 1:50 | 0 |

### Catalyst characteristics

*a. Electron microscopy*

In order to reveal the nature of the active centers of hydrogenolysis catalysts, a gas-phase HDC reaction was performed. It allowed identification of active intermediate catalyst forms, which probably cannot be detected in the liquid-phase reaction. In the latter case the samples may quickly degrade because of the reaction medium, which contains organic solvents and alkali.

During our study the catalyst samples were examined via transmission electron microscopy (TEM). According to the TEM data, before the gas-phase HDC reaction of $CCl_4$ the average size of supported metal particles of 1% $Pd_{90}Pt_{10}$/C was 35Å, while their post-reaction size was 67Å. This means that the size of the supported particles almost doubled during the reaction. Electron microphotographs of 1% $Pd_{90}Pt_{10}$/C are shown in Figures 2 and 3.

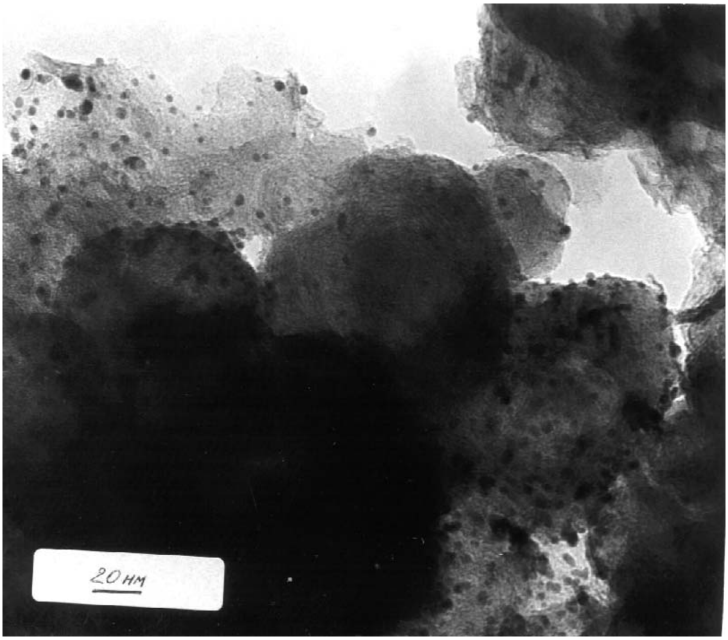

Fig. 2. Starting catalyst 1% $Pd_{90}Pt_{10}/C$.

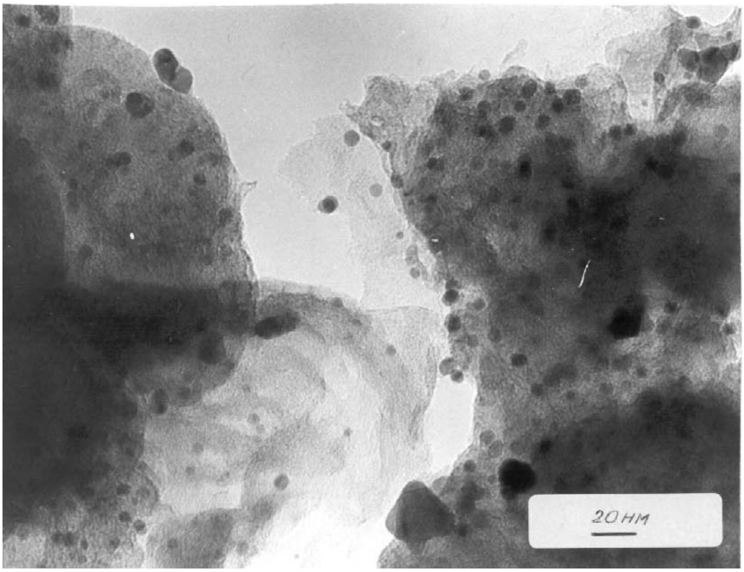

Fig. 3. Catalyst 1% $Pd_{90}Pt_{10}/C$ after gas-phase HDC of $CCl_4$.

*b. X-ray diffraction*

The prepared catalyst samples were analyzed by X-ray diffraction (XRD). The XRD data are listed in Table 3. In addition to the reported phases, a diffraction maximum with interplanar spacing = 4.15 Å was registered for a few samples. The maximum refers to traces of precursors of the active component, which were not completely reduced. Question marks in the Table correspond to unidentified phases.

For the 1% $Pd_{90}Pt_{10}/C$ catalyst, after gas-phase hydrodechlorination of $CCl_4$, the diffraction pattern showed a peak with interplanar spacing = 3.18 Å, a value assigned to the NaCl phase. A similar diffraction pattern was described in [4]. Using the PCPDF database (card No. 18-0951), the XRD graph also allowed to identify a Pd hydride phase. It showed a non-stoichiometric composition $PdH_{1-x}$ with a cubic symmetry group Fm3m, as described in [7].

**Table 3. XRD data for supported Pd - Pt hydrodechlorination catalysts.**

| Catalyst | Lattice parameter, Å | CSR size, Å | Phase |
|---|---|---|---|
| 1%$Pd_{90}Pt_{10}$ (T) before the reaction | 3.905 | 60 | Pd – Pt solid solution |
| 1%$Pd_{90}Pt_{10}$ (T) after gas-phase HDC of $CCl_4$ | 3.996(2) | 80 | NaCl + hydride |
| 1%$Pd_{90}Pt_{10}$ (T) after 30 min of gas-phase HDC of $CCl_4$ | ? | ? | Solution +hydride? (double peak) |
| 1%$Pd_{90}Pt_{10}$ (T) | 3.912 | 70 | Pd – Pt solution |
| 1%$Pd_{85}Pt_{15}$ (T) | 3.910 | 75 | Pd – Pt solution |
| 1%$Pd_{80}Pt_{20}$ (T) | 3.907 | 50 | Pd – Pt solution |
| 1%$Pd_{65}Pt_{35}$ (T) | 3.907 | 90 | Pd – Pt solution |
| 1%$Pd_{50}Pt_{50}$ (T) | 3.913 | 120 | Pd – Pt solution |
| 1%Pd (T) | 3.885(5) | - | Pd |
| 1%Pt (T) | 3.923 | 50 | Pt |
| 1%$Pd_{50}Pt_{50}$ | 3.938 | 40 | ? |
| 1%$Pd_{90}Pt_{10}$ | 3.951 | 55 | ? |
| 1%$Pd_{90}Pt_{10}$ (T) after gas-phase HDC of CB | 3.909 | 60 | Pd – Pt solid solution |

The XRD data indicates that the Pd-Pt solid solution particles are likely to be the active component of the supported Pd-Pt catalysts, which undergo the temperature treatment. The XRD results also confirm the formation of hydride phases after gas-phase hydrodechlorination of $CCl_4$. Hydride palladium forms are generated in the course of gas-phase HDC, though they were not detected in the catalysts during the liquid-phase process. This is possibly due to their quick degradation during the hydrogenolysis.

The presence of hydride forms allows assuming that the hydrodechlorination reaction proceeds by a mechanism of oxidative addition, for which the formation of hydrides was credibly ascertained [8, 9, 10].

The fact that the NaCl phase is present in the 1% $Pd_{90}Pt_{10}/C$ catalyst, after gas-phase hydrodechlorination of $CCl_4$, proves that the catalyst incorporates sodium ions. Unlike the techniques of catalyst doping with alkali metal ions cited in [4], the $Na^+$ introduction occurs during the reduction step of precursors of the active component with $NaBH_4$.

A few XRD patterns for the 1% $Pd_{90}Pt_{10}/C$ catalyst - before the reaction start and at different steps of gas-phase hydrodechlorination of $CCl_4$ - are shown in Fig. 4.

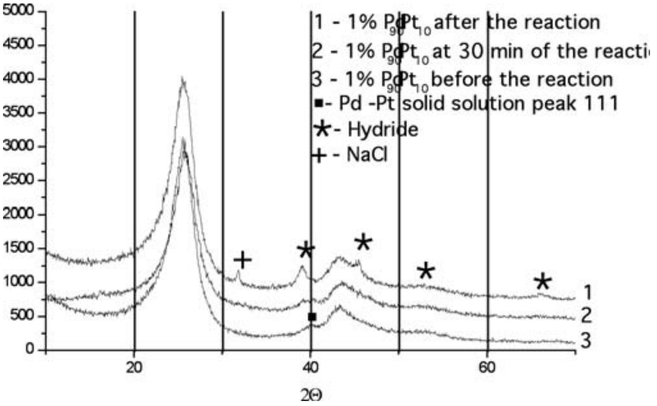

**Fig. 4. Diffraction patterns of catalysts 1%$Pd_{90}Pt_{10}/C$ before the reaction and at different steps of gas-phase hydrodechlorination of $CCl_4$.**

During the step of catalyst reduction by sodium boron hydride, the modification of the active component by boron, which is not XRD-detectable, may also occur. Table 4 provides the elemental analysis data obtained earlier for the same catalysts [11].

**Table 4. Elemental analysis data for the supported catalysts reduced by $NaBH_4$.**

| Catalyst | Concentration of the element, % | Composition |
|---|---|---|
| Ni/C | Ni – 3.71<br>B – 0.36 | $Ni_{67}B_{33}/C$ |
| $Ni_{98}Pd_2/C$ | Ni – 3.69<br>Pd – 0.14<br>B – 0.18 | $Ni_{78}Pd_{1,6}B_{20}/C$ |
| Pd/C | Pd – 3.01<br>B – 0.005 | Pd/C |

The tabulated data evidence that the supported catalysts include a boron admixture and its amount depends on the nature of supported metals. The presence of boron admixtures in supported bi- and monometallic catalyst samples will be further investigated in a dedicated research.

*c. X-ray photoelectron spectroscopy*

The following codes are used for the catalysts analyzed by XPES:

- *sample N1*: 3.5% $Pd_{90}Pt_{10}/C$ reduced by $NaBH_4$ and $H_2$ at 250°C after liquid phase hydrodechlorination of HB;
- *sample N2*: 3.5% $Pd_{90}Pt_{10}/C$ reduced by $NaBH_4$ and $H_2$ at 250°C;
- *sample N3*: 3.5% Pd/C reduced by $NaBH_4$ and $H_2$ at 250°C;
- *sample N4*: 3.5% Pt/C reduced by $NaBH_4$;
- *sample N5*: 3.5% Pd/C reduced by $NaBH_4$;
- *sample N6*: 3.5% $Pd_{90}Pt_{10}/C$ reduced by $NaBH_4$.

The identification of admixtures in the samples was based on an analysis of the plan spectra. The analysis showed only sodium admixtures (relative concentrations are given in Fig. 5).

The data about the calculated chemical composition of the catalyst surfaces is summarized in Table 5.

The chemical composition of the supported system $(Pt_xPd_{1-x})/C$ based on the XPES data was calculated as atomic %.

The analysis of the XPE spectra regarding the Pt4f and Pd3d core levels allows assuming that the chemical state of both platinum and palladium is homogenous and predominantly metallic. At the same time, the XPE spectra of the Pd-Pt catalysts show a number of specific features. There are a line shift in the spectrum of Pd and Pt core levels and a recharge effect for sample N2, as well as some variations of the Auger-parameter of Pd that evidences its heterogeneity.

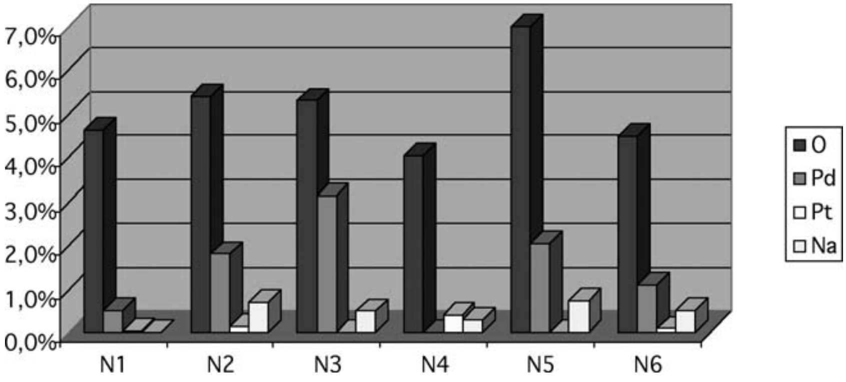

**Fig. 5. Diagram of the chemical composition of the samples.**

These particularities of the XPE spectra for sample N2 (5% $Pd_{90}Pt_{10}/C$ reduced by $NaBH_4$ and $H_2$ at 250°C) evidently result from the emergence of solid solutions and hydrides on the catalyst surface.

**Table 5. Chemical composition of the surface calculated on the XPES data basis.**

| No. of sample | Pd | Pt | O | Na | C | Pd/Pt |
|---|---|---|---|---|---|---|
| *N1* | 0.5 | 0.04 | 4.6 | 0.0 | 100 | 12.6 |
| *N2* | 1.8 | 0.2 | 5.4 | 0.7 | 100 | 11.0 |
| *N3* | 3.1 | 0.0 | 5.3 | 0.5 | 100 | - |
| *N4* | 0.0 | 0.4 | 4.0 | 0.3 | 100 | - |
| *N5* | 2.0 | 0.0 | 7.0 | 0.7 | 100 | - |
| *N6* | 1.1 | 0.1 | 4.5 | 0.5 | 100 | 10.7 |

A review of the experimental data led to the following assumptions. The palladium remains inactive in HDC of chlorobenzene under test conditions until the addition of platinum, which magnifies its activity. The inactivity of Pd can be explained by the electron interaction of supported metals. The XRD data for the Pd-Pt catalysts reduced both at room temperature and at 250°C allows presuming that, in the case of catalyst reduction by sodium boron hydride followed by heating, the activated components are solid solutions characterized by a nanometric distribution of metal particles. The higher activity of the heating-reduced samples for the hydrogenolysis of chlorobenzene is probably due to the greater homogeneity of the alloy system, which allows a closer electron interaction of the supported metals.

On the base of XRD and XPES data, it is possible to conclude that during reduction by boron hydride the catalysts are modified by sodium ions, which react releasing hydrogen chloride during the initial reaction steps. This evidently is one of the factors enhancing the stability of the supported catalysts during the hydrodechlorination reaction.

The results of the present research suggest the following HDC reaction mechanisms under the test conditions. A reaction scheme for the catalyst reduced without participation of $NaBH_4$ is shown in Fig. 6 [8, 9, 10]. Chlorobenzene adsorption on palladium leads to the generation of palladium chloride particles from metal particles and palladium hydrides (1), i.e. catalyst active centers are being etched as affected by releasing chlorine ions. For this reason, a constant feed of hydrogen to the catalyst is needed to realize the active component regeneration step (2).

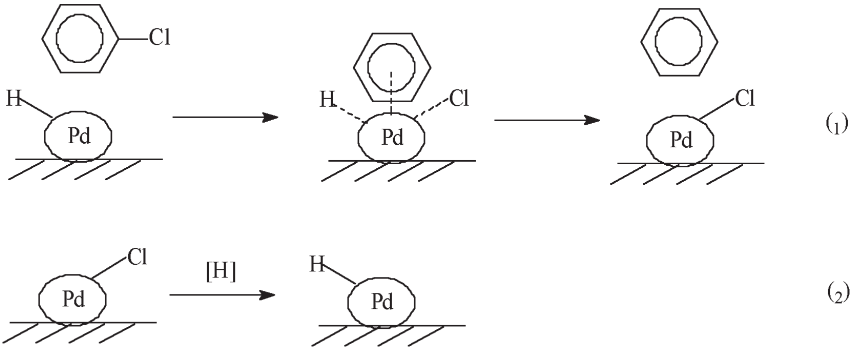

Fig. 6. Scheme of HDC of chlorobenzene on supported palladium particles.

A scheme of the reaction with the catalyst modified by sodium ions - during the reduction of the active component by boron hydride – is shown in Fig. 7. The scheme illustrates the assumption that sodium ions interact with releasing hydrogen chloride during chlorobenzenes adsorption on the catalyst surface in the initial reaction steps. This is obviously one of the factors that enhances catalyst stability in the hydrodechlorination reaction.

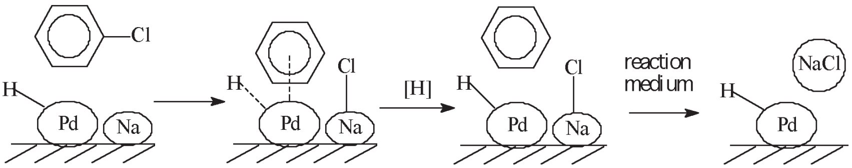

**Fig. 7. Scheme of the initial step of HDC of chlorobenzene on supported palladium catalysts modified by sodium.**

The experimental results lead to the following conclusions:

1. Bimetallic catalysts exhibit high activity in reactions of hydrodechlorination of chlorobenzene and hexachlorobenzene. A sequence of bimetallic catalyst activity has been obtained:
Pd-Pt > Pd-Fe ≈ Pd-Co > Pd-Ni.
2. The dependence of supported nanodispersed bimetallic catalyst activity on the Pd/Pt ratio was examined. It has been found that catalyst activity increases in a non-additive way after introduction of Pt (5.7-23 atomic %).
3. The XRD and XPES data confirmed that hydride forms are generated on the catalyst surface during the hydrodechlorination reaction.
4. The NaCl phase presence in the catalyst samples after hydrodechlorination has been ascertained by the XRD method; Na ions on the catalyst surface were detected using the XPES technique. These data allow assuming that sodium is incorporated into the catalyst composition during the stage of catalyst reduction by $NaBH_4$.

## REFERENCES

1. L.B. Zanaveskin, V.A. Aver'yanov. Advances of Chemistry, 67 (8), 1998.
2. C.A. Marques, M. Selva, P. Tundo, J. Chem. Soc. Perkin Trans. 1 (1993) 529-533.
3. C.A. Marques, O. Rogozhnikova, M. Selva, P. Tundo, J. Mol. Cat. 96 (1995) 301.
4. M.A. Aramendia, R. Burch, I.M. Garcia, A. Marinas, J.M. Marinas, B.W.L. Souhtward, F.J. Urbano, Appl. Catal. B 31 (2001) 163-171.
5. J.F. Moulder, W.F. Stickle, P.E. Sobol et al., (Eds.), Handbook of X-ray photoelectron spectroscopy, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie Minnesota, (1992).
6. V.I. Nefedov. X-Ray Electron Spectroscopy of Chemical Compounds. Handbook, Moscow, Khimia. (1984) 256.

7. Natl. Bur. Stand. (US) Monogr. 25, 5, 72 (1967).
8. S.T. Srinivas, P.S. Sai Prasad, P. Kanta Rao, Catal. Lett. 50 (1998) 77-82.
9. B. Coq, F. Figueras, In Proceedings of the Soviet-French Seminar on Catalysis, Novosibirsk, (1990) 218.
10. M. Yale, C. Keen, N.A. Bell, P.K.P. Drew, M. Cooke, Appl. Organometallic Chem. 9 (1995) 279.
11 V.I. Simagina , V.A. Yakovlev, V.A. Likholobov, React. Kin. Cat. Lett. 62, 1 (1999) 177.

# INTRODUCTION OF A BASE METAL AS A METHOD FOR IMPROVEMENT OF PD/C CATALYTIC ACTIVITY IN HYDRODECHLORINATION OF ECOTOXICANTS

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Hydrodechlorination (HDC) is the most promising method for useful modifications of chlorine organics [1, 2]. This reaction has currently found applications in many industrial processes, in the preparatory organic synthesis, like fluorohydrocarbons from chlorofluorohydrocarbons and nitrobenzenes from chloronitrobenzenes [1]. HDC allows not only toxic waste recycling, but also recovery of valuable products for their further reuse in industry. For example, HDC of $CCl_4$ yields chloroform and non-chlorinated $C_{2+}$ hydrocarbons.

The most active catalysts in HDC reactions are the ones based on supported palladium [2, 3, 4]. However, their high costs hamper industrial applications of these catalysts. In order to reduce such costs some modifications of Pd catalysts may be applied. A few methods are described in literature: the employment of metal hydrides in combination with the Pd catalyst [5, 6], introduction of additional components into the support [7, 8, 9], and introduction of additional metals into the active component [10].

A promising and already widely implemented method of catalyst modification is the dilution of the noble metal present in the active component using a second metal: Fe, Ni, Pt, etc. High performance bimetallic catalysts often include two noble metals (e.g. Pd-Pt and Pd-Au) [11-14]. Yet more attractive appear to be bimetallic catalysts containing a non-noble base metal, since their use allows reduction of costs. In this case the modifier metal does not necessarily need to be active in HDC reactions. Palladium catalysts are so expensive, that in order to reduce their contribution to the total cost of the process, it may be acceptable to use a bimetallic catalyst, even if it is somewhat less active than the monometallic one.

This research dealt with the effects on catalytic activity of Pd/C when Fe and Ni are used as additives for multiphase HDC reactions. In this study 1,4-Dichlorobenzene (1,4-DCB), 1,3,5-trichlorobenzene (1,3,5-TCB), hexachlorobenzene (HCB) and 2,4,8-trichlorodibenzofuran (2,4,8-TCDBF) were used as substrates. These polychlorinated compounds cause a high environmental concern. Hexachlorobenzene is a well-known insecticide. It is included in the list of the 12 most persistent organic pollutants (the so-called "dirty dozen") proposed in 1994 at the meeting of delegates from the USA, Canada, Japan and a few EU states. In Russia, it was utilized as a prophylactic treatment for wheat seed. Studies about the toxic properties of HCB showed that, like polychlorobiphenyls, it is a dioxin-like toxicant [15, 16]. HCB accumulates in mammals and exhibits carcinogen-, teratogen-[1], and immunotoxicant-like features. In order to examine the opportunities of bimetallic catalyst applications for HDC of ecotoxicants, such as dibenzodioxanes and dibenzofurans, a non-toxic congener (2,4,8-trichlorodibenzofuran) was selected as a model.

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1. Teratogen is a term indicating chemicals or physical factors, which may cause anomalous development of the fetus, malformations and other abnormalities.

All the catalysts were prepared by impregnation of the support (activated carbon, 1200 m$^2$/g) with a solution of metal nitrates and subsequent reduction by molecular hydrogen at 300$^{\mathrm{O}}$C. The reaction was carried out in liquid phase, under multiphase conditions. The reaction mixture composition was: 6 ml of substrate in hexane or isooctane (0.5 mmol substrate), 6 ml of 5% KOH (aqueous solution), 0.26 mmol of Aliquate 336 (tricaprylmethyl ammonium chloride), 0.1 g of the catalyst. An hydrogen flow was run through the system (5 ml/min). The advantages of the multiphase conditions and the role of the phase transfer agent were described in [17, 18].

The conversion value after a reaction time of 220 minutes was chosen as a benchmark to compare the catalyst activity. This parameter allows credible measurement of the conversion value even in the presence of low-activity catalysts. Details about the products of HDC of 1,4-DCB in the presence of Pd/C and Pd-Fe/C, after 220 minutes, are reported in Table 1.

The introduction of Fe into the active component of the catalyst led to a dramatic buildup of the 1,4-DCB conversion. For example, the addition of 4% Fe to the active component of the 1% Pd/C catalyst induced a 6.5-fold conversion increase (Table 1). Among the tested catalysts with different Pd:Fe ratios, maximum activity was displayed by 11% $Pd_7Fe_4/C$ (Pd:Fe = 7:4). In this case, full transformation of 1,4-DCB to benzene occurred after only 130 minutes.

**Table 1. Conversion and selectivity of multiphase HDC of 1,4-DCB over Pd-Fe/C catalysts after 220 minutes ($m_{cat}$ = 0.1 g, 45oC, Aliquate 336, hexane, 5% KOH).**

| Catalyst | Conversion, mol.% | Selectivity, mol.% | |
|---|---|---|---|
| | | Benzene | Chlorobenzene |
| 1% Pd/C | 9 | 10 | 90 |
| 5% $Pd_1Fe_4/C$ | 66 | 14 | 86 |
| 5% $Pd_4Fe_1/C$ | 26 | 15 | 85 |
| 6% $Pd_4Fe_2/C$ | 41 | 3 | 97 |
| 12% $Pd_{10}Fe_2/C$ | 38 | 5 | 95 |
| 11% $Pd_7Fe_4/C$ | 100* | 100 | 0 |

** - after 130 minutes.*

It should be outlined that the activity value was affected by the Pd:Fe ratio rather than by the Pd amount. It may be assumed that the activity tends to increase along with the amount of Pd. Yet, quite the opposite was observed in our case. At the ratio Pd:Fe = 1:4, the conversion value was 66% and when Pd:Fe = 4:1 it appeared to be as low as 26%, although the Pd content in the catalyst increased 4-fold. Note that the catalyst with 10% of Pd (12% $Pd_{10}Fe_2/C$) was less active than the one with 1% Pd (5% $Pd_1Fe_4/C$).

The Pd/C modification by Fe also resulted in an activity rise for HDC of 1,3,5-trichlorobenzene. Fig. 1 clearly shows that the activity of bimetallic catalysts is much higher than that of Pd/C. The introduction of Ni to the catalyst led to an even higher activity build-up, if compared to Pd-Fe/C. The pattern of 1,3,5-TCB conversion is given in Fig. 2. It is also important to highlight that the kinetic curves actually coincide (■ and ◆ in Fig.2) when the catalysts at the ratios of Pd:Ni = 8:2 and 5:5 are employed. Thus, it is possible to replace about 40% of Pd with Ni in the catalyst without significant changes in the catalyst activity. Such result is obviously of high practical value.

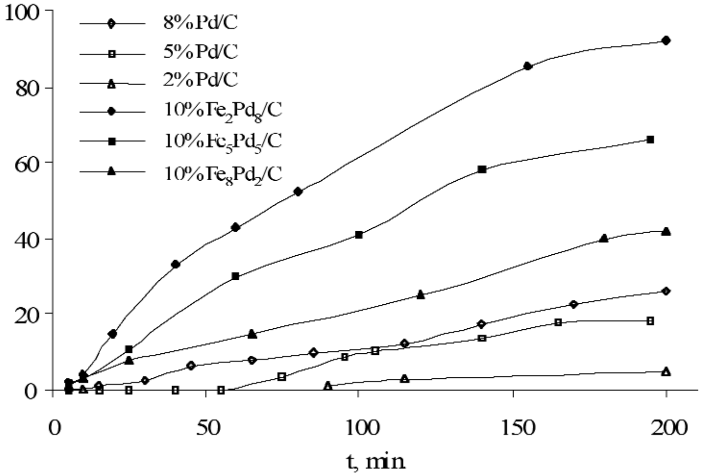

Fig 1. Conversion pattern for multiphase HDC of 1,3,5-trichlorobenzene over Pd-Fe/C and Pd/C catalysts (50°C, Aliquate 336, isooctane, 5% KOH).

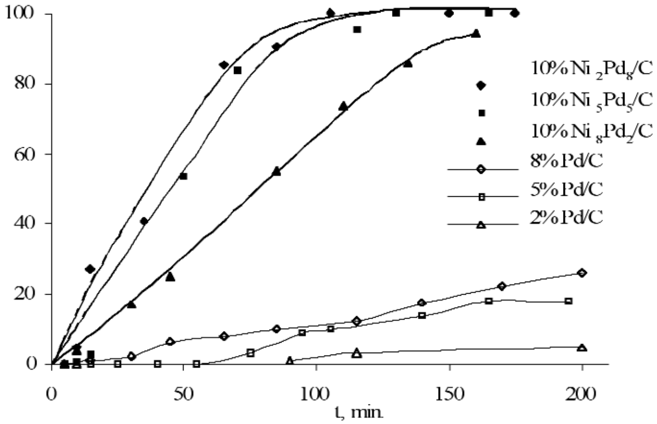

Fig 2. Conversion pattern for multiphase HDC of 1,3,5-trichlorobenzene over Pd-Ni/C and Pd/C catalysts (50°C, Aliquate 336, isooctane, 5% KOH).

A similar result was obtained for HDC of hexachlorobenzene over Pd-Fe/C (Fig. 3). The activity of the Pd/C catalysts increased according to the Pd content. Complete HDC of hexachlorobenzene with 8% Pd/C was achieved after 230 minutes. As in the case of Pd-Ni/C, the kinetic curves matched when the Pd:Fe ratios were 5:5 and 8:2.

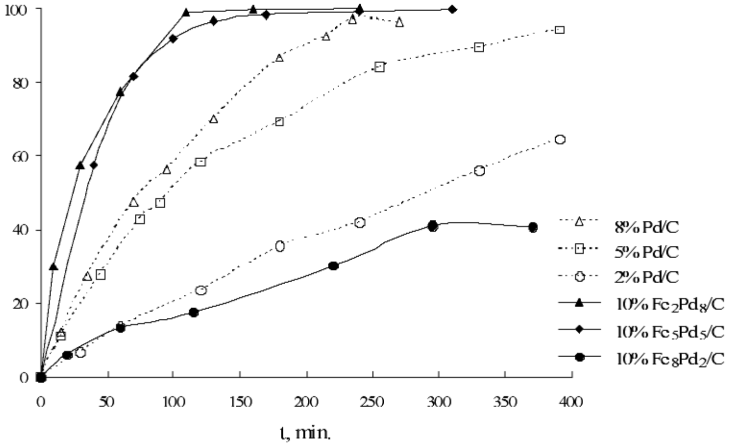

**Fig 3. Conversion pattern for multiphase HDC of hexachlorobenzene over Pd-Fe/C and Pd/C catalysts (50°C, Aliquate 336, isooctane, 5% KOH).**

Fig. 3 shows that the introduction of iron did not entail an activity rise in all cases. The Pd/C catalyst was less active when Fe was used in a large proportion (8%). Over 2% Pd/C, the HDC conversion was 60% after 400 minutes of reaction. Differently, in the presence of 10% $Pd_2Fe_8$/C it was as low as 38%. Under the HDC reaction conditions, the formation of iron chloride in a bimetallic catalyst is thermodynamically favoured with respect to $PdCl_2$ [11, 19-21]. Hence, iron acts as a chlorine acceptor and then the introduction of iron lowers the deactivation degree of the Pd catalyst. At the same time, fast encapsulation of Pd by an iron-chloride layer may occur at a high Fe percentages. This process results in an activity decline for the catalysts with a high Fe content.

Bimetallic systems with a higher activity were selected as catalysts for multiphase HDC of 2,4,8-trichlorodibenzofuran. The ‘conversion vs. reaction time’ curves for catalysts with different metal proportions are shown in Fig. 4. The activity of Pd/C rises as the Pd content grows from 5 to 8%. The addition of Fe to the catalyst led to a drastic reaction rate increase in both cases. For instance, in the presence of 8% Pd/C a full conversion of 2,4,8-TCDBF is reached after 240 minutes, while with 10% $Pd_8Fe_2$/C only 100 minutes are needed.

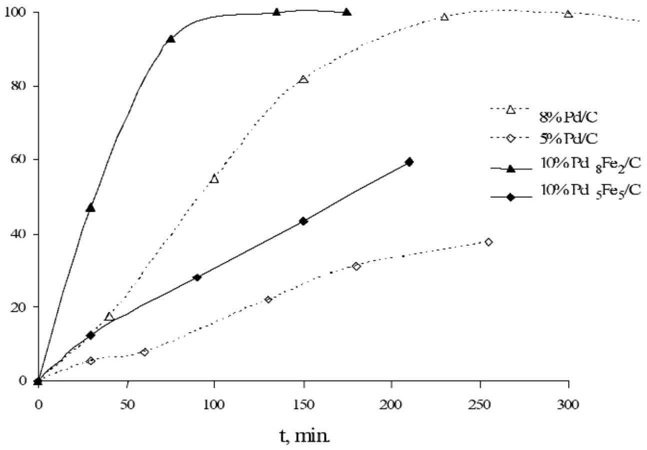

**Fig 4. Conversion pattern for multiphase HDC of 2,4,8-trichlorodibenzofuran over Pd-Fe/C and Pd/C catalysts (50°C, Aliquate 336, isooctane, 5% KOH).**

Thus, the prepared catalysts exhibited high activity during the reaction of multiphase HDC of chlorinated benzenes, including hexachlorobenzene and 2,4,8-trichlorodibenzofuran. The activity growth in the presence of bimetallic catalysts may be related to a few factors: (1) a Pd dispersion increase due to dilution by the second metal [20], (2) the alloy generation on the catalyst surface [22, 23], and (3) a Pd poisoning decline, due to the preferential chlorination of the second metal [11, 19-21]. An interaction of all the mentioned factors is quite probable in the studied system.

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## REFERENCES

1 Zanaveskin L.N., Aver'yanov V.A., Treger Yu.A. Advances of Chemistry, 1996, v. 65 (7), p. 667
2 Lunin V.V., Lokteva E.S. Izv. AN. Ser. chem., 1996, 7, p.1609
3 Pinder A.R. Synthesis, June 1980, p. 425
4 Urbano F.J., Marinas J.M. J. Mol. Catal. A, 2001, v. 173, p. 329
5 Simagina V.I., Litvak V.V., Stoyanova I.V., Yakovlev V.A., Mastikhin V.M., Afanasenkova I.V., Likholobov V.A. Russ. Chem. Bull., 1996, v. 45 (6), p. 1321
6 Simagina V.I., Mastikhin V.M., Yakovlev V.A., Stoyanova I.V., Likholobov V.A. J. Mol. Cat. A: Chemical, 1995, v. 101. p. 237
7 Wang Ch.-B., Lin H.-K., Ho Ch.-M. J.Mol.Catal. A General 2002, v. 180, p. 285
8 Srinivas S.T., Sai Pasad P.S., Kanta Rao P. Catal. Lett., 1998, v. 50, p. 77
9 Gampine A., Eyman D.P., J.Catal. 1998, v. 179, p. 315

10 Coq B., Figueras F. J.Mol. Catal. A Chemical, 2001, v. 173, p. 117

11 Kulkarni P.P., Kovalchuk V.I., d'Itri J.L. Appl.Catal. B Environmental, 2002, v. 36, p. 299

12 Malinowski A., Juszczyk W., Pielaszek J., Bonarowska M., Wojciechowska M., Karpinski Z. Stud.Surf.Sci.Catal., 2000, v. 130, p. 1991

13 Fujikawa T., Idei K., Ohki K., Mizuguchi H., Usui K. Appl.Catal. A General, 2001, v. 205, p. 71

14 Vadlamannati L.S., Kovalchuk V.I., d'Itri J.L. Catal.Lett., 1999, v.58, p. 173

15 Yufit S.S. *Toxins around us. A course of lectures*. James Publishers, Moscow, 2001, 400 p.

16 Shmidt Ch.W. Environmental health perspectives, 1999, v. 107, p.A18

17 Marques C.A., Selva M., Tundo P. J.Org.Chem., 1993, v. 58, p. 5256

18 Tundo P., Perosa A. Reactive & Functional Polymers, 2003, v. 54, p. 95

19 Baddeley C.J., Bloxham L.H., Laroze S.C., Raval R., Noakes T.C.Q., Bailey P. Surface science, 1999, v. 433-435, p. 827

20 Lingaiah N., Uddin Md.A., Muto A., Sakata Y. Chem.Commun., 1999, p. 1657

21 Luebke D.R., Vadlamannati L.S., Kovalchuk V.I., d'Itri J.L. Appl.Catal. B Environmental, 2002, v. 35, p. 211

22 Pinna F., Selva M., Signoretto M., Strukul G., Boccuzzi F., Benedetti A., Canton P., Fagherazzi G. J.Catal, 1994, v. 150, p. 356

23 da Silva A.B., Jordao E., Mendes M.J., Fouilloux P. Appl.Catal. A General, 1997, v. 148, p. 253

# HYDRODECHLORINATION AS A UNIVERSAL GREEN ALTERNATIVE FOR DESTRUCTION OF CHLORINATED PERSISTENT ORGANIC POLLUTANTS (POPS)

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In this research, green chemistry principles were applied to detoxication processes for polychlorinated organics and to some other chemical reactions performed using new types of solvents. Particularly, under the INTAS Project (grant #2000-00710), we evaluated the potential of the hydrodechlorination (HDC) reaction as a key method for the destruction of hazardous chlorinated compounds. Some aspects concerning the employment of ionic liquids (IL) as alternative solvents in liquid-phase chemical reactions have been also investigated.

This paper provides a summarized review of the performed HDC researches. A more detailed discussion of the results obtained in the researches on HDC of polychlorinated biphenyls (PCB) and IL in the reactions of CH-acids and polychlorinated compounds will be presented in two future publications.

## RESULTS AND DISCUSSION

During previous studies, P. Tundo *et al.* developed an efficient HDC technique for polychlorinated substances. In this method Aliquat 336® is used in combination with a heterogeneous catalyst and a 'water-nonpolar solvent' system (multiphase conditions) [1, 2]. The objective of our project was to examine the HDC process in details, both under the conditions proposed by Tundo and in alcohol-based media. The latter are widely utilized for reduction of organic compounds. Table 1 reports HDC data for a model substance – 1,4-dichlorobenzene (DCB) – in various alcohols.

**Table 1. HDC of 1,4-dichlorobenzene over 10% Pd/C under hydrogen flux at room temperature in various alcohols.**

| No. | Solvent | Reaction time, min | Conversion, % |
|---|---|---|---|
| 1 | Methanol (abs) | 15 | 68 |
| | | 30 | 100 |
| 2 | Ethanol (abs) | 20 | 79 |
| | | 55 | 100 |
| 3 | n-Propanol | 20 | 87 |
| | | 45 | 100 |
| 4 | Isopropanol | 30 | 100 |
| | Isopropanol* | 150 | 38* |
| 5 | n-Butanol | 60 | 100 |
| 6 | Tret-butanol | 60 | 30 |
| | | 300 | 86 |

**: with addition of Aliquat 336 (0.2 mmol)*

**Table 2. HDC of chloroaromatic compounds over 10% Pd/C under hydrogen flux at room temperature in isopropanol.**

| No. | Substance | Reaction time, min | Conversion, % - end product |
|---|---|---|---|
| 1 | 1,2,4,5-Tetrachlorobenzene | 50 | 100% - benzene |
| 2 | Hexachlorobenzene | 60 | 100% - benzene |
| 3 | Pentachlorophenol | 75 | 100% - phenol |
| 4 | PCB | 150 | 100% - biphenyl (72%) |
| 5 | PCB (Sovol) (mean composition corresponds to pentachlorodiphenyl) | 330 | 100% - biphenyl (98%) |

As can be seen from Table 1, the DCB transformation into benzene proceeds in alcohol-based media under mild conditions and with high conversion rates. The two maximum values were found in methanol and isopropanol.

This method was successfully used for reduction of a number of other polychlorinated aromatic molecules (Table 2).

This method well integrates a multiphase HDC process, that we employed for reduction of pesticides, including lindane [3], aldrin, dieldrin [4, 5], DDT, polychlorinated dibenzo-p-dioxins, and furans [7] (Table 3).

It can be reasonably anticipated that different modifications of the proposed HDC method will be usable for detoxication of other polychlorinated pollutants, included in the Stockholm Convention list (endrin, chlordane, mirex, toxafene, heptachlorine, etc.) and further chlorinated organic toxicants.

**Table 3. Hydrodechlorination of some POPs included in the Stockholm Convention over 10% Pd/C under hydrogen current at room temperature in isopropanol.**

| Substance | Conversion % / time |
|---|---|
| Dieldrin | 100% / 5 min |
| Polychlorobiphenyls (PCB) | 100% / 40 min |
| Hexachlorobenzene (HCB) | 100% / 80 min |
| Pentachlorophenol * | 100% / 75 min |
| Lindane* | 100% / 10 min |

**: Not included in the list of 12 POPs specified by the Stockholm Convention.*

Thus the proposed HDC method allows neutralization of all 12 POPs included in the Stockholm Convention (2002) and probably several dozens of other polychlorinated substances included in the list of the Persistent Toxic Substances (PTS).

An important issue is the evaluation of the toxicant destruction degree. Naturally it is desirable to achieve the complete destruction of a chlorinated substance (the absence of the original toxicant is controlled by chromatography-mass-spectrometry of the reaction mass). However, the destruction of the majority of a toxicant (e.g. 99%) should also be considered as a positive result. The single mandatory requirement set forth by the Stockholm Convention is that the reaction has to be performed in such a way not to release polluted wastes into the environment (solvents, wastewater, gas emissions or solid waste). If the process complies to this rule, it can be used and its final products – containing residual PTS amounts - will be included in the total PTS balance, when a national PTS inventory is made. For instance, if 99% of the about 20,000 tons of the PCB stock officially registered in Russia is destroyed, the remaining 1% will be only 200 tons, this implies a major improvement for the Russian environment. In addition, some other technologies, even more expensive, could be selected for destroying such minor PCB quantities. Note that these arguments do not apply to dioxins due to their extreme toxicity.

An ancillary condition of the Stockholm Convention demands that PTS are to be destroyed in a manner that will absolutely prevent generation of new toxicants. The proposed HDC method perfectly meets this requirement because the toxicity is caused by halogen atoms. The elimination of chlorine (bromine) atoms and their substitution with hydrogen atoms lead to a loss of toxic properties in PTS. For example, HDC of a PCB mixture yields a single product - biphenyl - which is not toxic. HDC of the pesticide DDT does not produce toxic DDE; aldrin and dieldrin transform to chlorine-substituted intermediates that lose chlorine in the following phases of the reaction. Lindane behaves in a similar manner: during HDC it is converted into low-toxic chlorobenzenes, which gradually transform into benzene. An exception is pentachlorophenol because its HDC yields phenol, which is assigned to rather toxic substances. Yet, phenol is a commercial product and does not fall under the Stockholm Convention. Thus the pentachlorophenol-to-phenol transformation puts it outside of the Convention lists.

## CONCLUSIONS

The collected experimental data evidence that the HDC technology is a universal solution for implementing dechlorination of chlorinated aromatic and chlorinated aliphatic compounds. The method allows their detoxication under mild conditions and ensures high degrees of neutralization for hazardous molecules.

## REFERENCES

1 C.A. Marques, M. Selva, P. Tundo. J. Chem. Soc., Perkin Trans. I (1993) 529.
2 C.A. Marques, M. Selva, P. Tundo. Facile HDH with $H_2$ and Pd/C catalyst under multiphase conditions. 2. Selectivity and kinetics” JOC 1994, 59, 3830-3837.
3 S. Zinovyev, N Shinkova, A Perosa, P.Tundo “Degradation and Transformations of Lindane via the Multiphase Catalytic Hydrodechlorination over Pd/C and Raney-Ni” *Appl. Cat. B: Env,* 2003, (submit)
4 S.Zinovyev, N.Shinkova, P.Tundo “Multiphase catalytic hydrodechlorination of polychlorinated substrates over Raney-nickel”, *Remediation Technologies*, 2002, p.75-77;
5 S. Zinovyev, N Shinkova, A Perosa, P Tundo “Hydrodechlorination of polychlorinated organics over supported catalysts and Raney-Ni under multiphase conditions” 7th International HCH and Pesticides Forum, June 5-7, 2003, Kiev, Ukraine

6 Green Chemistry in Russia. V. Lunin, E. Lokteva, and P. Tundo, Editors. Green Chemistry Series n° 12. Published by INCA Consortium, Venice, 2005. 160 pp.

7 S.ZINOVYEV, P.TUNDO Multiphase catalytic hydrodechlorination: destruction of toxic organochlorine compounds under mild conditions. Organohalogen compounds, 2002, 72-74.

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