REVIEW
submitted by Prof. Silviya Zhivova Todorova
Institute of Catalysis - Bulgarian Academy of Sciences
(member of the scientific jury)
on the dissertation of Dr. Yuri Angelov Kalvachev
Full Professor at the Institute of Catalysis of the Bulgarian Academy of Sciences,
Entitled "**Synthesis and Properties of Zeolite Catalysts**",
submitted for obtaining the scientific degree
"Doctor of Chemical Sciences"

I. Documents submitted

Prof. Dr. Kalvachev represented the all necessary documents required by Law for the scientific degree "Doctor of Science":

- Dissertation;
- Abstract;
- Diploma for completed higher education;
- Diploma for obtaining the scientific-educational degree doctor;
- Diploma for acquiring the academic position professor;
- Scientific CV;
- Record of the session of the Colloquium of the Institute of Catalysis, as well as copies of the scientific papers included in the dissertation.

II. General presentation of the candidate

Prof. Dr. Kalvachev graduated from the National Mathematical High School, a class teaching chemistry in 1981. He received his higher education in 1988 at Sofia University "St. Kliment Ohridski ", Faculty of Chemistry with a master's degree in analytical and organic chemistry, after which he became a PhD student in the Department of Organic Chemistry of the same faculty. In 1992 he defended his dissertation on "Study of the interaction of alcohols with zeolites type pentasil and molecular sieves type SAPO". Since 1992 he has been working at the Institute of Catalysis (IC-BAS). Consecutively holds the position of assistant proffesor II-I st. 1993-1997. In the period 1997 to 2007 he is Assistant Professor I degr. At IMC-BAS. He was elected "Associate Professor" at the same institute in 2007. In 2017, he won a competition for "professor" at the Institute of Catalysis. Prof. Kalvachev has specialized in a number of prestigious universities. He was a postdoctoral fellow at the Japan Science and Technology Agency - National Research Institute in Osaka; postdoctoral fellow with Texaco grant from the University of Ghent, Belgium, Faculty of Inorganic Chemistry; postdoctoral student of the foundation "Al. von Humboldt ", University of Leipzig.

Prof. Kalvachev's expert activity is expressed in the following: member of the Standing Subcommittee "Research and Technological Development" at the Monitoring Committee of the Operational Program "Science and Education for Smart Growth" 2014-2020; Deputy Chairman of the Temporary Scientific Expert Committee on Bilateral Cooperation of the NSF, 2016-2017; evaluator under the Operational Program "Development of the Competitiveness of the Bulgarian Economy 2007-2013". He is a member of the organizing committees of Humboldt Kolleg.

Prof. Kalvachev is the project coordinator of 9 projects: 1 project funded by NATO, 1 by 6 FRAMEWORK PROGRAM (Prof. Kalvachev is a module leader), 2 projects in the framework of bilateral cooperation with the Romanian Academy, 5 projects with the Bulgarian National Science fund. The attracted funds for these projects are over BGN 1,200,000. He is the coordinator of the module "Mobility" in the project under OP "Human Resources Development" on "Support for the development and implementation of doctoral students, postdoctoral students and young scientists in the field of materials science, mineralogy and crystallography", funded by the European Social Fund.

He organized a specialized course "Infrared spectroscopy" (30 hours of lectures) at the PhD Training Center of BAS. The course is organized annually in the period 2010-2015. For the period 2013-2015, Prof. Kalvachev is the supervisor of two PhD students. He is the leader (mentor) of over 20 students under the Operational Program Development of Human Resources - "Student practices" -BG051PO001-3.3.07-0002, 2013-2014. The students are from different universities: Sofia University "St. Kliment Ohridski", NBU, MGU" St. Ivan Rilski ", University of Plovdiv. Prof. Kalvachev has also contributed to the academic growth of many scientists from various scientific organizations. He was a member of the jury for the defence of dissertations and the jury for the academic positions of "Professor" and "Associate Professor".

III. General description of scientometric indicators

The scientific publications included in the thesis are 27 in total, including one book chapter, three patents and 22 publications in a scientific journals. All of the presented publications are in leading journals in the field of micro- and mesoporous materials and materials science such as *Microporous and Mesoporous Materials, J. Mater. Sci; High performance polymers; Cryst. Growth Des, Applied Catalysis B - Environmental; Journal of Catalysis; Catalysis Communications; Materials Letters.* The distribution of publications by quartiles is as follows: in Q1-9 publications, Q2-5 publications, Q3-2 publications, Q4-2 publications and four lower ranked publications. Prof. Kalvachev is also the author of a chapter from the book Synthetic Micro-and Nanocrystalline Zeolites for Environmental Protection Systems in "Nanoscience Advances in CBRN Agents Detection", NATO Science for Peace and Security Series A. The three patents have been issued in Japan, USA and Bulgaria. Thus, the total number of points on indicator D is 469 and is significantly above the required minimum, which is 100.

The total number of citations on the publications included in the dissertation is 273. All citations are from foreign authors in prestigious international journals. The total number of points on indicator D is 546, which exceeds the recommended criteria. The results from the dissertation are presented at 58 scientific forums, with 31 poster presentation and 27 oral.

Personal participation of the author

I am impressed by the volume of research, which is an indication of diligence and dedication to scientific research. My assessment of the author's personal participation in the dissertation research is based on the content of the dissertation and my personal impressions. The abstract and the analysis of the current state of research on the problem area shows that

prof. Kalvachev is very familiar with the available literature, which helped him to plan clearly and accurately the scientific research and to choose methods and approaches to achieve the goals of the dissertation. After reading the dissertation, I am deeply convinced that he knows the problem thoroughly. The dissertation includes the work of two doctoral students, which in no way diminishes the value of the research, but only shows the candidate's ability to be a successful supervisor and mentor.

V. Abstract

The abstract is written according to the requirements and accurately reflects the main scientific contributions of the dissertation.

VI. The relevance of the problem

Zeolites are aluminosilicate widely used in a number of industrial processes, such as adsorbents, catalysts or catalyst carriers. They are used in the oil refining and petrochemical industry, for the production of detergents, dryers for separation and purification of gas mixtures, in ecology. The wide use of zeolites is due to their two main properties, - the selective sorption of molecules of different sizes and easy ion exchange. One major disadvantage of zeolites is that their ordered microporous channel system sometimes leads to diffusion limitations of the reagents, which reduces their efficiency.

The thesis of Prof. Kalvachev is focused on a very interesting topic, namely the study of the catalytic properties of zeolites and materials with zeolite structure and the influence of structure, particle size, chemical composition, conditions and modifications on the catalytic properties. The zeolite modification in most cases is made by environmentally friendly synthetic procedures. Part of the dissertation is also aimed at developing an environmentally and cost-effective method for the synthesis of zeolite from coal ash.

VII. Scientific contributions

Prof. Kalvachev's scientific activity is focused on the development of synthetic techniques for obtaining micro- and mesoporous materials, their modification depending on the purpose of their application, application of various physicochemical methods for their characterization. The main scientific contributions of Prof. Kalvachev cover the following areas: Synthesis of nanoscale zeolites and hierarchical structures; Synthesis of titanosilicates and catalytic properties of gold supported on mesoporous titanosilicates; Synthesis and catalytic properties of zirconosilicates and zirconium-modified zeolites; Synthesis and properties of hybrid zeolite-polymeric materials; Zeolites synthesized from coal ash and study of their adsorption and catalytic properties.

As mentioned above, one major disadvantage of zeolites is that their ordered microporous channel system sometimes leads to diffusion limitations of the reagents, which reduce their efficiency. Over the last decade, much effort has been focused on the synthesis of zeolites, in which access to catalytically active centers is facilitated and diffusion constraints are reduced. One way to achieve this goal is the synthesis of zeolites with particle in the submicron and nanometric regions (nanoseolites). The interest in nanoseolites stems come from the possibility of fine-tuning surface and structural properties by varying the crystal size,

morphology, active surface. Nanozeolites are increasingly used in areas that are not traditional for zeolites, such as optical thin films, membranes, chemical sensors, etc. In the dissertation different approaches for synthesis of nanosized zeolites are used, such as soft synthesis conditions (temperature below 120ºC); variation of the water content in the starting gel; addition of nuclei to the starting gel. The use of the latter method produces high siliceous zeolites without the use of an organic structure directing agent, and it is also possible to form structures with different Si /Al ratios that is not possible to obtain by other methods.

For the first time the method of vapor phase transformation of starting gels for synthesis of zeolite type LTA was applied. Using both methods - low-temperature hydrothermal crystallization at 30-60 ºC and vapor-phase transformation of starting gels, zeolite A crystals with a size of less than one micrometer are obtained.

The synthesis of mordenite was performed without the presence of an organic structure directing agent. The size of the zeolite particles in the synthesis of mordenite was controlled by varying the reaction parameters - water content in the starting gel, temperature, amount of added seeds. The addition of seeds leads to other economic and environmental advantages - increasing the rate of synthesis, high yield, obtaining pure zeolite phases.

Nanosized zeolite Beta was synthesized using seeds. This allows for a wide variation of the Si /Al ratio, reduction of the synthesis time and obtains products in the nanoscale range (100-400 nm). The zeolite Beta was obtained successfully by combining synthesis in a fluorine medium using seeds. Thus, a sample was obtained without significant defects in the crystal lattice and with small particles in the nanometric region - 200-300 nanometers and improved catalytic properties in the m-xylene transformation reaction and increased selectivity for the desired isomerization products (ortho and para-xylenes).

Pure crystalline zirconosilicates were obtained for a relatively short period (1-5 days) without the use of organic structure directing agent. The optimization of the conditions for the synthesis in the Na_2O-ZrO_2-SiO_2-H_2O system was used. Layered silicate kenyaite is also obtained in this system. It is used as a support for catalysts for the oxidation of volatile organic compounds - *n*-hexane and benzene. Kenyaite-based catalysts exhibit higher catalytic activity than silica-supported one due to the higher dispersion and lower interaction of the supported metal oxides with the support.

Zeolite X is synthesized from coal ash using a two-stage process - fusion of the ash with sodium hydroxide and subsequent hydrothermal synthesis. It was found that the adsorption capacity of the zeolite thus obtained is comparable to that of NaX zeolite obtained from pure chemicals, which makes it very suitable for CO_2 adsorption and creation of TPPs with "zero emissions" - without ash deposition and without release of CO_2. Deposition of platinum on such a zeolite produces catalysts which are active in the oxidation of carbon monoxide.

For the first time, by treatment with a buffer solution of hydrofluoric acid and ammonium fluoride zeolites mordenite and ZSM-5 (aluminum and gallium samples) with secondary porosity were obtained. This buffer is not highly selective for the silicon atom or the heteroatom, and thus the Si/T atom ratio is almost preserved in the final product. Zeolites with secondary porosity have a higher catalytic activity in the m-xylene transformation reaction than the starting samples. This is also the case in the glycerol esterification reaction, in which hierarchical zirconia-modified hierarchical mordenite is used as a catalyst.

For the first time, a gold-based catalyst supported on mesoporous titanosilicate Ti-MCM-41 was used to oxidize propylene to propylene oxide in the presence of oxygen and hydrogen. A synergistic effect has been established between gold and titanium, and only their simultaneous presence in the catalyst leads to the reaction. It is suggested that a hydroperoxy particle is formed during the reaction, which is the active agent for the oxidation of the hydrocarbon. The catalyst is also active for the oxidation of propane to acetone and isobutane to tert-butanol.

Materials for medical use have been development based on zeolite L. The materials are low-toxic, biocompatible and their antibacterial properties are comparable to an antibiotic substance. The antibacterial properties are due to the ion exchange silver in zeolite L. Based on this zeolite, a controlled release material for the drug enalapril maleate (EM) has been developed. The results of this study show a higher release profile for EM in the case of the formula APV-PU-ZL-EM / 40: 15: 20: 25, which may be recommended to be included in pharmaceutical compositions for oral administration.

I have a one question to prof. Kalvachev: which of the two considered methods for overcoming diffusion problems when using zeolites in catalytic processes is more reliable and more appropriate - the use of nanoscale zeolites or hierarchical zeolites.

Conclusion

The thesis contains scientific and applied results, which represent an original contribution to science and meet all the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for the application of LDASRB of the Ministry of Education and the respective Regulations of BAS, as well as the specific requirements of the Institute of Catalysis -BAS. The dissertation shows that Prof. Dr. Yuri Angelov Kalvachev has in-depth theoretical knowledge and professional skills in the scientific specialty "Chemical Kinetics and Catalysis".

All facts represented above giving me justification to give my positive estimate and to recommend convincingly to the members of the Scientific Jury to award the degree of "Doctor of Science" to Prof. Dr. Yuri Angelov Kalvachev in scientific field 4. "Natural Sciences, Mathematics and Informatics", professional field 4.2 "Chemical Sciences", scientific research specialty "Chemical Kinetics and Catalysis".

Sofia, 02. 07.2021 Prof. PhD Silviya Todorova