REVIEW

by Prof. Georgi Nikolov Vayssilov

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of a dissertation entitled

"Synthesis and properties of zeolite catalysts"

presented by Professor Dr. Yuri Angelov Kalvachev

for awarding the scientific degree "Doctor of Science"

The dissertation is presented for the award of the scientific degree "Doctor of Science" by Prof. Dr. Yuri Kalvachev, professor at the Institute of Catalysis at BAS. Prof. Kalvachev graduated from the Faculty of Chemistry of Sofia University "St. Cl. Ohridski" in 1988 as a MSc in Organic and Analytical Chemistry. After a regular doctorate in the Department of Organic Chemistry of the same faculty, in 1992 he defended his doctoral dissertation on "Study of the interaction of alcohols with pentasil type zeolites and molecular sieves type SAPO" with scientific supervisor Prof. Ts. Bezouhanova. From 1992 to 1994 he was appointed a specialist chemist in the IONH and IC at BAS, and from 1994 to 1999 he was a research associate at IC at BAS. During the period 2000 - 2007 he was a research associate 1st degree at the IMC at BAS, where in 2007 he was elected associate professor. In 2017 he won a competition for a professor of chemical kinetics and catalysis at the Institute of Catalysis at the Bulgarian Academy of Sciences, where he still works.

Prof. Kalvachev specialized in three long-term specializations as a postdoctoral fellow at the National Research Institute in Osaka, Japan, in 1996-1997, and at the University of Ghent, Belgium, in the period 1998-1999. From 2000 to March 2002, he was a fellow of the Alexander von Humboldt Foundation at the University of Leipzig, Germany.

According to the presented information, the scientific contributions of Prof. Kalvachev have been published in 67 scientific publications in referenced scientific journals and he is a co-author of 4 patents. His publications have been cited 472 times, and according to the web of science, his h index is 12.

The dissertation for the award of the degree of Doctor of Science, presented for review, includes the candidate's research aimed at clarifying the properties and applications of zeolites and the various methods for obtaining synthetic zeolites. The dissertation summarizes scientific results published in 24 scientific publications and three patents. 18 of

the publications are in impact factor journals, of which 9 are in Q1 and 5 in Q2. Six publications are in conference proceedings, book chapters or other scientific journals. The dissertation is written on 146 pages, which includes the summarized scientific contributions of the author based on the research described in the dissertation (4 pages) and a list of scientific publications, on which the dissertation is based (3 pages). The results of the research in the dissertation are presented with the following parts: Introduction (3 pages), Basic parameters determining the catalytic properties of zeolites (8 pages), Synthesis and catalytic properties of nanosized zeolite crystals and hierarchical structures (34 pages), Synthesis of titanosilicates and catalytic properties of gold deposited on mesoporous titanosilicates (7 pages), Synthesis and catalytic properties of zeolite materials modified with zirconium (18 pages), Zeolites synthesized from coal ash (19 pages), Synthesis of properties and of hybrid zeolite-polymeric materials (17 pages), Abstracts (3 pages), and References (14 pages). The dissertation includes 73 figures, 15 tables and cites 289 references.

After the Introduction of the dissertation, part 2 presents a brief overview of the main characteristics of zeolites, their composition and structure. The factors determining the adsorption and catalytic properties of zeolites and their selectivity, as well as the main types of active centers in them are described. Examples are given of the most commonly used zeolite structures in practice and of the methods for their study.

Part 3 of the dissertation is the largest in volume and presents the candidate's research on the synthesis and modification of nanosized zeolite crystals and hierarchical zeolite structures, as well as their catalytic applications. Special attention is paid to the mechanism of crystallization of zeolites, and on this basis the factors determining the formation of nanosized crystals are analyzed. The most commonly applied synthetic approach by Prof. Kalvachev is the use of seeds for zeolite crystallization, through which nanosized crystals of zeolite beta and mordenite are obtained.

The preparation of hierarchical zeolite crystals is one of the modern issues in the field of zeolite synthesis in the world, as in those materials a significantly larger part of the zeolite surface is available to the molecules of the reagents due to reduced diffusion limitations. By this reason together with the preserved catalytic activity and selectivity of this type of zeolite materials, the industry is showing considerable interest. Prof. Kalvachev's research on the preparation of hierarchical zeolites includes treatment of the zeolite with a mixture of hydrofluoric acid and ammonium fluoride, in which the formation of mesopores in the

zeolite crystal does not lead to a change in the Si/Al ratio in the zeolite structure, which is often a problem when the classical methods are used - by treatment with an alkaline base or with acid alone.

Part 4 of the dissertation describes the results related to the preparation of catalysts for selective oxidation based on titanium-containing zeolites and mesoporous materials. In the framework of these studies different types of microporous, mesoporous and layered materials containing titanium in the crystal lattice were synthesized, which was proven by appropriately selected methods. Prof. Kalvachev is among the pioneers in the preparation of gold nanoparticles deposited on titanium-containing zeolites or similar materials and their application for selective oxidation of alkenes to the corresponding oxirane derivatives. These results, some of which were obtained during his specialization in the group of Prof. Haruta in Japan, are the basis of two of the patents included in the dissertation.

Part 5 of the dissertation includes studies of catalytic systems containing layered silicate. These materials with added platinum and / or cobalt oxide as the active phase are used as environmental catalysts for the oxidation of volatile organic compounds, benzene and hexane, which are industrial pollutants.

The next part 6 also has an environmental aspect, as it describes methods for using waste coal ash for zeolite synthesis. The idea is related to the significant amount of silicates in the ash, which are necessary for the synthesis of zeolites. In a series of studies, methods have been developed for the synthesis of faujazite-type zeolite and its application as a carbon dioxide adsorbent or as a platinum carrier as an active phase for the oxidation of carbon monoxide.

Part 7 of the dissertation includes studies for the preparation and applications of composite organic-inorganic materials containing zeolite crystals and polymer. Nano-sized zeolite crystals embedded in a polymer matrix are used to prepare these materials, and various procedures for preparing the composite material are described. The obtained zeolite-polymer films have been studied for various potential applications - as antibacterial agents (when using zeolites exchanged with silver ions), as systems for transport and separation of drugs (based on nanosized zeolite L crystals), and as polymeric films with high strength and thermal stability.

The conclusions presented in part 8 of the dissertation accurately reflect the results of the research described in it.

I appreciate the research included in the publications that have been submitted for review. The presented research is original and most of results have practical application, as can be concluded from the patents of which Prof. Kalvachev is a co-author. The purposeful choice of methods for synthesis, modification and characterization, specific for the selected zeolite systems, as well as for their use is impressive.

According to the terms in the Law for the development of academic staff, the proposed dissertation and scientific publications included in it can be viewed as a "monograph or publications in specialized journals equivalent to the monograph" and "other original scientific - research publications".

I know the candidate personally and my impressions of him and his research and results are excellent.

In conclusion, the dissertation presented by Prof. Dr. Yuri Kalvachev for the awarding the scientific degree "Doctor of Science" and his scientific contributions meets the requirements of the Law, the Regulations for its application, and Rules of terms and conditions for acquisition of scientific degrees and for holding academic positions at the Institute of Catalysis – BAS, for obtaining the scientific degree "Doctor of Science" . The candidate is a leading specialist in the field of synthesis and modification of zeolites, the study of their properties and their applications in adsorption, catalysis and preparation of hybrid materials. Based on the above, I recommend that the scientific jury appointed by order of the director of the Institute of Catalysis – BAS, to award to Professor Dr. Yuri Angelov Kalvachev the scientific degree "Doctor of Science" in the professional field 4.2. Chemical sciences, scientific specialty Chemical kinetics and catalysis.

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Prof. Georgi N. Vayssilov