

## ATTITUDE OF REVIEWER

by prof. Dr. Anton Naydenov  
Institute of General and Inorganic Chemistry (BAS)

member of the scientific jury, elected by the decision of the Scientific Council of Institute of Catalysis (BAS), Protocol 5 on 29.04.2021. and the order is no. RD-09-36/29.04.2021. about the competition for participation in the scientific degree "Doctor of Science" in the professional direction 4.2. "Chemical Sciences" and the scientific specialty "Chemical Kinetics and Catalysis" with the candidate professor. Dr. Yuri Angelov Kalvachev.

The dissertation of Professor Dr. Yuri Angelov Kalvachev entitled "Synthesis and properties of zeolite catalysts" has been written on the basis of a summary of the results of 27 scientific papers with a volume of 128 pages, and the number of cited literature sources is 289.

In general, the research of Professor Dr. Yuri Kalvachev is aimed at developing new methods for the synthesis of micro- and mesoporous materials, methods for their characterization and appropriate modification for their future application in practice. As a result of the research activity of Prof. Dr. Yuri Kulvachev showed that using the method of low-temperature hydrothermal crystallization and vapor-phase conversion of the initial gels for the synthesis of zeolite of the LTA type, zeolite A crystals with a size of one micrometer can be obtained, which has a significantly smaller size compared to the initial sample prepared under normal hydrothermal conditions and an analog output gel. It was found that as a result of changing the reaction parameters, conditions for controlling the particle size of the obtained zeolites can be realized. For example, in the synthesis of mordenite and beta-zeolite, the raw particles have reduced sizes, and the approach affects the synthesis rate, yield, and purity of the resulting material. It was shown that when using fluorine ions in combination with the use of nuclei in the synthesis of Beta-zeolite, a sample was obtained without significant defects in the crystal lattice and with small particles of the order of 250 nanometers. The measurement represents a high catalytic activity in the m-xylene transformation reaction. It was shown that it is possible by treatment with buffer solution of hydrofluoric acid and ammonium fluoride to obtain zeolite samples with secondary porosity, finding that this buffer is weakly selective to silicon atoms or to the heteroatom, which allows the final product to maintain the ratio between silicon and the heteroatom atoms.

It is shown that gold deposited in the mesopores of titanosilicate is an active catalyst for oxidation by oxygen of propylene to propylene oxide in the presence of hydrogen. The synergistic effect between gold and titanium is established and the presence of the element in the catalyst is the only condition for proceeding of the reaction. The proposed explanation is that during the reaction formation of hydroperoxy particle, which is an active agent for oxidation of propylene. In addition, it is proved that the catalyst is also active for the oxidation of propane to acetone and isobutane to butanol.

Prof. Dr. Yuri Kalvachev proposed an approach in which the size of the zeolite crystal size is controlled by varying the water content in the initial gel, which permits the ensuring of conditions for limitation the space of growing of single crystals and lower solubility of specific type of nucleos in favor to other types. As an alternative, crystals at desired phase are added thus aiming to their role as nucleos in the initial gel. It is established that the achieve decrease in the crystal size is result from the large number if introduced nucleos for growing the crystals. The described method permits the preparation of highly silicon – containing without the use of organic organic structure-determining reagents. The combined effect between the synthesis in fluorine medium and the use of nucleos during the synthesis on zeolite type Beta showed that it was possible to obtain a sample without significant defects in the crystal lattice, but with a small particle size.

The proceeding within the synthesis in highly alkali medium brought to the formation of large number of defects in the crystal structure, which negatively affects the catalytic activity.

These defects are related to the uneven distribution of aluminum in the zeolite lattice and the presence of silanol "nests". In order to avoid these disadvantages, it is proposed to work in a fluorine medium when a fluorine anion is used as a mineralizing agent. As a result of the research, a method has been proposed that combines the fluorine medium with the presence of nucleos up to 10 wt. %. The particles obtained by this method are nanometric in size, and the catalytic tests in the m-xylene transformation reaction showed a higher degree of conversion than the sample synthesized in an alkaline medium. It has been shown that the application of additional sulphation of mesoporous zirconia enhances its acidic properties, making it a suitable catalyst for isomerization, in this case for cumene cracking. As a continuation of the research in this direction, zirconium dioxide deposited on mordenite as a support was obtained. Experiments were performed in a glycerol esterification reaction with potential adhesion as a biofuel. In this case, the proposed main idea is that mordenite is treated for secondary porosity. The catalytic activity is higher and the deactivation is much slower when the treated support is used. The selectivity to the most valuable product triacetyl glycerol is the highest - nearly 70%.

It has been found that mesoporous materials could be used as drug carriers for the purpose of controlled release of the medicinal product from the body. It has been found that the time of absorption by the body can be changed by varying the pore size, which allows to control the time of action of the drug substance.

Professor Dr. Yuri Kalvachev is working on the search for optimal conditions for the synthesis of zircon silicates obtained in the  $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2-\text{H}_2\text{O}$  system, the goal is to obtain pure crystalline products in a short period and without the use of organic reagents. It is found that along with the production of a somewhat pure zircon silicate phase, this system also produces a layered silicate keniaite, which is applicable as a carrier for catalysts for the oxidation of volatile organic substances. Developed is an alternative ammonia method for the deposition of platinum and cobalt, in which small particles are formed on the surface of the carrier. It was observed that the platinum modified samples has a higher catalytic activity in the complete oxidation reaction of benzene, however in the oxidation reaction of n-hexane no promoting effect from the use of platinum is noted. Significant achievement of professor Dr. Yuri Kalvachev is the synthesis of Beta-zeolite by using of fluorine ions in combination with the use of nucleos. The high catalytic activity of this material was demonstrated in the m-xylene transformation reaction, a higher activity than the sample synthesized in an alkaline medium being reported.

### Conclusion

The presented dissertation of professor Dr. Yuri Angelov Kalvachev fully meets the requirements of the announced competition for the award of the scientific degree "Doctor of Science" in the professional direction 4.2. "Chemical Sciences" and the Scientific speciality Chemical Kinetics and Catalysis. The presented results by Prof. Dr. Yuri Angelov Kalvachev cover the requirements in the rules of conditions and procedure for awarding the scientific degree "Doctor of Science" at the Institute of Catalysis (BAS). Therefore, I strongly recommend that the members of the respected scientific jury award the professor. Dr. Yuri Angelov Kalvachev scientific degree "Doctor of Science" in the professional direction 4.2. "Chemical Sciences" and scientific specialty "Chemical Kinetics and Catalysis."

Sofia, 28.05.2021.

Reviewer:

Prof. Dr. Anton Naydenov