OPINION

by Prof. Tatyana Tabakova, PhD, Institute of Catalysis – BAS

of the Doctoral thesis presented for awarding the degree "Doctor of Sciences"
in professional field 4.2 "Chemical sciences", scientific specialty "Chemical kinetics and catalysis"

Author: Prof. Yury Angelov Kalvachev, PhD, Institute of Catalysis – BAS
Topic: Synthesis and properties of zeolite catalysts

The set of documents presented by Prof. Kalvachev is in accordance with the Rules on the Terms and Conditions for Acquisition of Academic Degrees and Occupation of Academic Positions at Institute of Catalysis (IC) – BAS and meets the criteria of the IC – BAS for obtaining the degree "Doctor of Sciences". The dissertation presents a summary of the results that have been published in 24 scientific works and 3 patents, two of them are international, and have been presented at 58 scientific forums in Bulgaria and abroad. The number of noticed citations – 273 is an indication for the interest of the world scientific community. The results have been achieved during specializations after awarding grants from the Japan Agency for Science and Technology, Texaco - Belgium and "Alexander von Humboldt" Foundation - Germany, as well as during the implementation of 25 research projects with national and international funding, 9 of which have been coordinated by the candidate. Prof. Kalvachev is a supervisor of two successfully defended PhD students.

The dissertation of Prof. Kalvachev deals with the synthesis of zeolites and materials with zeolite structure aiming their use in heterogeneous catalytic reactions. A brief assessment of the importance of zeolite catalysis is made in the Introduction. The advantages of zeolite sorbents and catalysts and the main approaches for obtaining zeolite materials with a proper chemical composition, structure and particle size are indicated. The objective is well formulated and the tasks for its achievement are clearly outlined. Chapter 2 describes the main properties of zeolites, with an emphasis on those specific features that are crucial for achieving high catalytic activity. The next three chapters present the results of the application of innovative and knowledge-based procedures for the synthesis of nanosized zeolite crystals and hierarchical structures, mesoporous titanosilicates for application as supports of gold-containing catalysts, and zirconium-modified zeolites. Finding optimal, ecological and economic conditions for the synthesis of zeolites from coal ash, the study of their adsorption properties for the greenhouse gas CO_2 capture and their use as support of catalysts with high efficiency for the elimination of CO and volatile organic compounds (described in Chapter 6) is directly related to the global and very topical issue of air purity. The synthesis and study of the properties of hybrid zeolite-polymeric materials, discussed in the last chapter, also has an applied focus in the field of human health. Low degree of toxicity and antibacterial properties of zeolite with exchanged silver ions, included in the composition of biocompatible material for medical purposes, have been proven. Of special interest is also the use of zeolites in controlled drug release materials. An overview of the current state of the art and the existing challenges has been made in each chapter together with description of the results.

The contributions, which contain new and original scientific information, are related to pioneering approaches in application to specific synthetic techniques, varying of reaction parameters, addition of seeds, post-synthetic treatment with a buffer solution of hydrofluoric acid and ammonium fluoride, for synthesis of different type zeolites with significantly improved properties. An original

strategy for addition of seeds without the presence of an organic structure directing agent has been used that allows particles size control and has economic and environmental advantages. The thesis presents experimental evidences for improved catalytic activity and selectivity in the m-xylene transformation reaction due to the facilitated access to the active sites resulted from the secondary created porosity. The concentration of acid sites, their strength and the accessibility of reactants to them play a decisive role in the activity and selectivity of the materials studied toward toluene disproportionation. The catalyst behavior (activity and selectivity) of gold nanoparticles, supported on mesoporous titanosilicates has been studied for the first time in epoxidation of propylene, selective oxidation of propane to acetone and isobutane to t-butanol with a H_2–O_2 mixture in flow conditions.

The contributions with a clear potential for practical application address:

1. Development of a two-stage process for zeolite synthesis from coal ash. Based on the measured adsorption capacity with respect to CO_2, the thesis proves the possibility of utilization of coal ash from thermal power plants, thus solving important environmental problems. It is known that the disposal of large amounts of ash creates a risk of environmental pollution (soil, groundwater, air). The synthesis of zeolites from industrial waste leads to a reduction in the total cost of CO_2 capture. Economically profitable and promising is the application of zeolites as support of active catalytic materials for oxidation of CO and volatile organic compounds.
2. Synthesis and properties of hybrid zeolite-polymeric materials. The results outline attractive applications for medical and pharmaceutical purposes.

The reliability of the conclusions made about the relationship of the catalytic performance (activity and selectivity) and textural, structural, morphological, electronic properties is based on an in-depth analysis of the results by using of a complex of well-selected physicochemical methods (powder X-ray diffraction, scanning electron microscopy, high resolution TEM, FTIR, UV-vis and Raman spectroscopies, ^{29}Si и ^{27}Al NMR spectroscopy, texture analysis by low-temperature nitrogen adsorption) and catalytic measurements.

The abstract is well prepared and reflects properly the research performed and the results reported in the thesis.

I know Prof. Kalvachev from our joint work in the Institute of Catalysis as a colleague with significant theoretical knowledge and professional skills in experimental work and results interpretation. This dissertation is a confirmation of the high qualification and experience in the synthesis of zeolites, the application of original approaches for their modification, characterization and application in catalysis and other areas with practical importance. The contributions meet all the requirements of the Law for development of the academic staff in the Republic of Bulgaria, the Regulations for its implementation and the respective Rules of the IC - BAS. The volume and undoubtedly high quality and originality of the scientific contributions, revealed in the thesis, as well as the overall activities of the candidate, give me a compelling reason to vote positively and to recommend to the Honorable members of the Scientific Jury to vote for the award of the degree "Doctor of Sciences" in the professional field 4.2. „Chemical Sciences", scientific specialty „Chemical Kinetics and Catalysis" to Prof. Yury Kalvachev

Date 07.06.2021 Member of the Scientific Jury:

/Prof. Tatyana Tabakova, PhD/