REVIEW

Submitted by Prof. Dr. Silvia Zhivova Todorova, Institute of Catalysis-BAS regarding the materials presented by Assistant Professor Dr. Ivaylo Georgiev Tankov for participation in a competition for the academic position of "Associate Professor" at the University "Prof. Dr. Asen Zlatarov "- Burgas, professional field 4.2" Chemical Sciences ", scientific specialty" Chemical Kinetics and Catalysis ", announced in the Newspaper of State issue no. 95 of 16.11.2021

1. General presentation of the candidate's materials.

Assistant Professor Dr. Ivaylo Georgiev Tankov is the only candidate in the competition for the academic position of "Associate Professor". The set of materials submitted by the applicant is in accordance with Article 67 para. 2 of of the Regulations for the conditions and order for acquiring scientific degrees and occupying of academic positions in University "Prof. Dr. Asen Zlatarov, Burgas.

To participate in the competition, Dr. Tankov presented the necessary documents: a copy of the announcement in the State Gazette; CV; a copy of the diploma for "doctor"; document proving work experience; documents certifying the teaching activity with the included list of graduates, guided by the candidate, a copy of the developed curricula and a university textbook on electronic media; reference for fulfilment of the minimum requirements; research publications; list of citation; documents certifying the candidate's participation in projects; list for participation in scientific forums; reference on indicator 4 - Habitation work from "group B"; lists of scientific papers, citations, copies of scientific papers, list of participations in national and international conferences and congresses.

2. Short biographical data of the candidate.

Dr. Ivaylo Tankov was born on May 07, 1983 in Burgas. He completed his higher education in 2007 at the University "Prof. Dr. Asen Zlatarov "- Burgas with a master's degree in Chemistry and Technology of Oil and Gas. In the period June 2007 - April 2009 he worked as an operator - chemical processes to a company for the production of salts with pharmacopoeial purity. Since October 2009 he has been enrolled as a PhD student in the Laboratory of Catalytic Processes in Energy and Environmental Protection at the Institute of Catalysis at the Bulgarian Academy of Sciences. Scientific supervisors are Prof. Sonya Damyanova and Assoc. Prof. Dr. Katya Arishtirova. In 2013 he defended his dissertation with title "Preparation and characterization of catalysts for methane reforming with carbon dioxide." After successfully defending his doctoral thesis, Ivaylo Tankov was appointed an assistant at the University "Prof. Dr. Assen Zlatarov" - Burgas, and later was elected Assistant Professor at the same university where he is until now.

3. Evaluation of the scientific research works of the candidate

Dr. Tankov is a co-author of a total of 33 publications (31 in the journals with impact factor). He participate in the concurs with 15 publications. They are all in prestigious international journals in the field of materials science and catalysis, such as the *Journal of Molecular Liquids, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy; Journal of Molecular Structure, Fuel.*

The presented publications are divided into two groups, covering indicators **B** and **Г**, according to the Regulations on the terms and conditions for obtaining scientific degrees and for holding academic positions. In the first group, indicator **B** - "Habilitation work - scientific publications in publications that are referenced and indexed in world-famous databases of

scientific information (WoS or Scopus)", are presented 5 publications (four of them fall in Q1 and one in Q2), as the total number of points is 120 points, with a required minimum of 100 points. Dr. Tankov is the first author cn all published publications.

The second group comprises 10 publications (5-Q1 and 5-Q2), covering indicator **Г**, with a total of 245 points with the required 200 points. In the group of indicators **Д**, the requirements are also significantly exceeded - 100 points are needed, the candidate has 144 points. All citations are in prestigious international journals, which is in support of the importance and relevance of Dr. Tankov's research.

Dr. Tankov is a participant in the working groups of 1 international and 3 national projects. The international project is funded by the Interreg program for cross-border cooperation Bulgaria-Turkey. This shows that Dr. Tankov is very responsible for the tasks, which makes him a desirable participant in the work teams.

The dissemination of scientific results has been achieved through participation with oral and poster presentations in a number of national and international scientific meetings as follows: reports of international forums - 1 piece, reports of national forums - 1 piece, posters of international forums - 1 piece ., posters at national forums - 2.

4. Teaching activity

The teaching activity of the candidate is expressed in conducting lecture courses and exercises in several specialties, guiding graduates and participating in the development and renewal of 13 programs. The disciplines trained by Ivaylo Tankov are: Technology of Organic Synthesis, Reaction Kinetics and Catalysis (234 hours of lectures, 539 hours of exercises), Organic Chemical Technologies (42 hours of lectures 42 hours of exercises), Quantitative study of chemical reactions in petrochemical synthesis (136 hours of lectures, 91 hours of exercises), Renewable energy raw materials (150 hours of exercises), Metal complex and interfacial catalysis (270 hours of exercises), Kinetic methods for selection of the reaction unit (60 hours of lectures, 270 hours of exercises)), Fine Organic Synthesis (90 hours of lectures, 375 hours of exercises), Engineering solutions for clean and safe technologies (30 hours of lectures, 30 hours of exercises). Four graduates have completed their theses under the supervising of Dr. Tankov.

The scientific publications of Dr. Tankov are at an extremely high level, despite his busy teaching.

5. Scientific contributions

5.1. Habilitation work

The habilitation work is based on 5 articles, four of which are categorized in quartile Q1 and one in Q2 (articles 1,2,3,4 and 5 of the List of scientific publications of the candidate). This part includes scientific papers aimed at obtaining and characterizing new active and stable homogeneous and heterogeneous catalysts for esterification reactions. The following homogeneous catalysts were synthesized: pyridine hydrogen sulfate (PHS), pyridine dihydrogen phosphate (P2HP), pyridine nitrate (PN), 4-amino-1H-1,2,4-triazole nitrate (ATN).

Based on them, heterogeneous systems (PHS/Al_2O_3, PHS/RHA, xPHS/AC) were obtained by using supports with high specific surface area- Al_2O_3, rice husk ash (RHA) and activated carbon (AC). The obtained catalysts were studied with a set of modern physicochemical methods such as X-ray diffraction and X-ray phase analysis, X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FT – IR), ultraviolet and visible spectroscopy (UV-vis), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), adsorption porosimetry (SBET).

The catalytic activity of the synthesized samples was studied in the butyl acetate and methyloleate (biodiesel) synthesis. Papers related to the production of biodiesel are included in criterion **Г**. I find especially positive the fact that in addition to a complete characterization of the catalysts, mechanisms of the esterification reaction are presented and on the basis of these mechanisms, mathematical models for studying the kinetics and thermodynamics of obtaining the target products are derived. Quantum mechanical (DFT) analysis on the thermal and catalytic properties of the samples as a function of their molecular geometry, electronic structure and intramolecular interactions are significant part in the research area of Dr. Tankov. The complex study of catalytic materials was performed.

As is well known, esterification takes place in the presence of an acid catalyst through the formation of an active complex (transition state) from the catalyst-substrate interaction. Therefore, in order to get an idea of the catalytic behavior of ionic liquids in the reactions of butyl acetate synthesis (PHS, P2HP, ATN, TAHSSM and PN), a detailed analysis of their electronic structure was performed.

It was found that the catalytic activity in the esterification reaction increases with the increasing of the ionic liquids acidity. The evidence obtained is both through theoretical methods and through experimental ones. A detailed analysis of the pure atomic charges shows that the center with the highest positive charge in the structure of PHS, P2HP is the hydrogen atom bonded in the form of a hydroxyl group in $[HSO_4]^-$ and $[H_2PO_4]^-$. It is shown that the hydrogen atom located at the nitrogen atom in the aromatic ring has the lowest electron density (high positive charge) in ATN and PN. It was found that the electron density localized on hydrogen atoms decreases in the order ATN (+0.430)> PN (+0.463)> P2HP (+0.469)> PHS (+0.476) ≈ TAHSSM (+0.479). Since low electron density (significant positive charge) corresponds to a high degree of acidity, the theoretically calculated order of increase of pure atomic charges shows a complete coincidence with the experimentally established catalytic activity. The above order of increasing the degree of acidity was obtained experimentally.

In order to optimize the conditions of the esterification reaction, experimental, kinetic and thermodynamic studies were performed. It has been found that as the catalyst content increases, the ester yield and esterification rate constant increase as a result of increasing the quantity of the active centers.

The fact that the entropy of activation has a negative value is evidence that the mechanism of formation of butyl acetate and methyl oleate involves the formation of an active complex. Theoretical calculations show that the formation of the transition state is due to interaction between the hydrogen atoms of the catalyst.

The yield of butyl acetate increased in the order: 27% (PHS / α-Al2O3) <45% (PHS / AC) <51% (PHS / RHA) for heterogeneous catalysts which is accordance with the decrease in PHS particle size.

The main contributions from the habilitation work are:

- For the first time ionic liquids pyridine dihydrogen phosphate (P2HP), pyridine nitrate (PN), 4-amino-1H-1,2,4-triazole nitrate (ATN), pure or loaded on high surface support, are used as catalysts in the esterification reactions.
- For the first time has been described a mechanism for the production of butyl acetate in the presence of ionic liquid (PHS) catalyst. The mechanism involves the formation of an active complex.
- The optimal conditions for the production of butyl acetate and methyl oleate in the presence of PHS, ATN and PN have been established by kinetic and thermodynamic analysis.

36 citations of the publications included in the habilitation thesis were noticed.

5.2. Other publication

This section presents publications related to indicator **Г** (publications in journals that are peer-reviewed and indexed in world databases of scientific information (Web of Science and/or Scopus), not included in habilitation works). The total number of points is 245 points (200 points necessary). A total of 100 citations of these works have been noted.

Three main areas can be distinguished in this part:

- Preparation new ionic liquids and studying their composition and structure;
- Analysis of surface phenomena occurring in heterogeneous ionic liquids;
- Study of the kinetics of thermal decomposition of ionic liquids.

According my opinion the main contributions are listed below.

The ionic liquid pyridine dihydrogen phosphate (P2HP) was synthesized for the first time and its molecular geometry was established, as well as the aromaticity of an inorganic anion in the structure of ionic liquids was documented for the first time. For the first time, heterogeneous catalysts based on ionic liquids and supports with a high surface area Al_2O_3, rice husk ash (RHA) and activated carbon (AC) were obtained. The phase composition, the specific surface, the size distribution of the pores were determined, the particle size of the ionic liquid present on the surface was calculated. Changes in the phase composition were found after impregnation of α- Al_2O_3, RHA and AC with aqueous solution of ionic liquid PHS. Different types of PHS particles have been identified depending on the carrier. Agglomerates of PHS particles with an average size of 31.5 nm are present on the surface of α- Al_2O_3,, while agglomerates of PHS are not registered on the surface of RHA. PHS crystallites ranging in size from 6.3 to 14.8 nm depending on the amount of PHS applied were observed in the AC carrier.

The main achievements in the thematic area "Analysis of surface phenomena occurring in heterogeneous ionic liquids" are the following:

- For the first time, the vibrational bands in the ionic liquids PHS and TAHSSM and the heterogeneous catalysts obtained based on them (PHS/α- Al_2O_3, PHS/RHA TAHSSM/α-Al_2O_3 and xPHS/AC) were studied.
- The nature of the surface interactions in PHS/α- Al_2O_3, PHS/RHA, TAHSSM/α-Al_2O_3 and xPHS/AC as a function of the support type and the structure and location of the immobilized active phase on the surface in PHS/α-Al_2O_3, PHS/RHA and xPHS/A Csystems were established.

In the next thematic area the studies of the kinetics of thermal decomposition of ionic liquids are included. Studies of the thermal behavior of the following ionic liquids PHS, P2HP и PN and the heterogeneous systems obtained on their basis (PHS/α- Al_2O_3 and PHS/RHA) are presented for the first time. The mechanisms of melting and decomposition of the samples as a function of the degree of intramolecular hydrogen bonding and the nature of the support have been established. The kinetics of thermal decomposition of pyridine nitrate was studied for the first time.

6. Scientific and applied activity

The scientific-applied activity is expressed in a protected utility model, for which a Certificate of Registration with the Patent Office of the Republic of Bulgaria is available (Reg. № 4007 U1). The utility model refers to a temperature indicator with thermochromic composition for direct application to human skin in order to continuously monitor body temperature and a kind of visualization and indication.

Conclusion

I know the candidate personally because he was a PhD student at the Institute of Catalysis-BAS. My impressions of him are that he is characterized by extreme diligence,

discipline and dedication to work. He can work in a team with his own contribution and ideas. The scientific papers presented to me for review showed a significant growth of the candidate in scientific terms. I am impressed by the volume of research, which is an indication of diligence and dedication to scientific research.

The research of Assistant Professor Dr. Ivaylo Georgiev Tankov fully corresponds to the topic of the announced competition for awarding the academic position of "Associate Professor". The publishing activity and the citation on the published results prove that Dr. Ivaylo Tankov fully covers and exceeds all requirements of the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB) and the Regulations on the terms and conditions for obtaining scientific degrees and holding academic positions at the University "Prof. Dr. Asen Zlatarov "- Burgas. Therefore, I strongly recommend to the members of the Scientific Jury to award **Assistant Professor Dr. Ivaylo Georgiev Tankov** academic position **"Associate Professor"** in the professional field **4.2 "Chemical Sciences"** and scientific specialty **"Chemical Kinetics and Catalysis".**

Data 18. 03. 2022

Sofia

Member of the Scientific Jury:

/Prof. Silviya Todorova, PhD /