MASARYK UNIVERSITY
FACULTY OF SCIENCE
DEPARTMENT OF CHEMISTRY

Professor Jiri Pinkas, Ph.D.
Kotlarska 2
CZ-61127 Brno, Czech Republic
ph.: intl.+ 420549496493
fax: intl.+ 420549492443
e-mail: jpinkas@chemi.muni.cz

Brno, January 22, 2017

Reviewer's Report on the Habilitation Thesis

of Dr. Manoj B. Gawande

Synthesis of Advanced Nanomaterials: Catalytic and Sustainable Applications

The work of Dr. Gawande, summarized in his Habilitation thesis, is focused on the preparation and structural and spectroscopic characterization of nanocatalytic systems based on nanoparticles of metals, metal oxides, mixed-metal oxides and graphene oxide. These basic nanomaterial components are combined into structured multiphasic and multifunctional assemblies with controlled morphology and composition. They are subsequently used as catalysts in important chemical reactions. In the broader context, the work aims to the area of synthesis of advanced catalysts, exploration of the systems featuring multiple functionalities, such as catalytic and magnetic, and design of green and sustainable reaction systems. This field at the borderline of inorganic, organic, physical and materials chemistry is currently a research area of tremendous activity and extreme importance. Applications of benign, abundant and inexpensive materials are highly desirable in the light of future development of chemical industry, regulatory environment, and resource depletion.

The introductory part of the thesis succinctly introduces background information on homogeneous and heterogeneous catalysis and makes a point for design, synthesis and exploration of nanostructured catalysts that take advantages of both worlds and represent the best option in the development of new greener, more efficient, and sustainable catalytic systems. Further chapters focus on iron oxide based catalytic systems that should replace expensive and rare transition metals. Major attention is devoted to morphological control on micro-meso scale of iron oxide nanoparticles. A substantial part of the thesis describes successful construction of composite catalysts based on magnetic iron oxides and catalytically active metal or metal oxide nanoparticles anchored on their surface. Systems, such as magnetite or maghemite with Pd, NiO, CuO, and Au, are presented. An acidic catalyst was prepared by grafting sulfonic acid on the surface of the Fe_3O_4 nanoparticles. All these systems feature high catalytic activity, good recyclability, chemical stability, and easy magnetic separation form the reaction mixture. The other important category of prepared nanocatalysts is bimetallic core-shell nanoparticles, such as Pd-Pt and Ag-Ni. These can be used in colloidal suspension or supported on graphene oxide particles.

A few typing errors were marked directly in reviewer's copy of the habilitation thesis for candidate's information and editing. The formula NH_4OH should not be used as such species does not exist. A term aqueous solution of NH_3 sufficiently describes the situation. Several references are cited under different numbers which keeps the reader alert (9=36, 15=171, 24=35, 172=189).

MASARYK UNIVERSITY
FACULTY OF SCIENCE
DEPARTMENT OF CHEMISTRY

Questions for the habilitation thesis defense:

1. How the volumes of market sales of nanocatalysts were obtained. Such sales reports are quite expensive to obtain.

2. Experimental results from other laboratories and from theoretical calculations show that the core-shell Pt-Pd alloy nanoparticles are stable as a Pt-core/Pd-shell system. Data presented in this thesis identify an inverse arrangement with a Pd-core/Pt-shell structure. Please comment on how the one pot reaction could favor the formation of the thermodynamically unfavorable structure.

3. Similar situation is encountered with the Ag-Ni nanoalloy system. As the metals are completely immiscible and differ in sizes and surface energies, the most stable arrangement of a core-shell particle was calculated to be Ni-core/Ag-shell. However, here the solution thermolysis of Ni and Ag precursor mixture provides the inverse Ag-core/Ni-shell nanoparticles. What factors could govern this behavior and how the outcome could be influenced by reaction parameters.

This work is composed of 21 research and review papers and as a whole is focused on a very topical area of inorganic composite nanomaterials with multifunctional activity and a large application potential. Synthetic and catalytic studies brought us a number of new results and some previously unknown facts were discovered. The author demonstrated his ability to carry out synthetic experiments, a wide array of characterization measurements by structural and spectroscopic techniques, and catalyst evaluation. The author is also capable of analyzing obtained data and of drawing reasonable conclusion based on experimental facts. Figures, charts and graphs presented throughout the work are clearly rendered and convey information to the reader. The large number of topical references shows that the author possesses a good comprehension of the current status of the field and its recent developments. The large number of peer-reviewed publications demonstrate candidate`s ability to obtain and communicate scientific results of a high standard. Author published 62 research papers and reviews with over 1300 citations. Of these reports, 31 were published while working in Olomouc and they gained so far more than 400 citations (w/o self-citations). Several of these papers are marked in the WOS as Highly cited papers. His H-index is 26.

In conclusion, I can declare that, the overall amount and quality of this work is excellent and exceeds requirements for habilitation thesis. I recommend this work to be **accepted** in partial fulfillment of requirements for awarding a docent degree.

Jiri Pinkas, Ph.D.
Professor of Inorganic Chemistry