UNIVERSITY OF BUCHAREST

FACULTY OF CHEMISTRY

HETEROGENEOUS CATALYSIS - A PILLAR OF THE GREEN CHEMISTRY AND SUSTAINABLE DEVELOPMENT

HABILITATION THESIS

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ABSTRACT

The Habilitation thesis present the most important scientific achievements obtained in fine chemicals synthesis and biomass valorization areas, after my PhD defense, in 2001.

Catalysis is clearly one of the foundational pillars of Green Chemistry and it will continue to be one of the main vehicles that take the chemical enterprise into a future of sustainability. For this, the production of chemicals, nowadays based on catalysis (ca. 90% of chemicals produced *via* catalytic routes), should have to move from homogeneous to heterogeneous catalysis (whenever possible) in order to avoid product contamination, reduce the processing costs, enhance the recovery and favor recyclability of catalysts. Therefore, with the aim to improve older industrial processes or to initiate other nowadays new processes under a greener manner, novel selective efficient solid catalysts were created and developed.

The most important envisaged fine chemicals synthesis were selected from those which still raises environmental problems at industrial level through the generated wastes and high energy consumption, as E and K vitamins synthesis and menthol synthesis. The most important part of this research direction which I conducted as an Alexander von Humboldt fellow, under the guidance of Prof. Erhard Kemnitz, at Humboldt-Universität zu Berlin, and many years after my return, at University of Bucharest, lead to the discovery of a new class of catalysts (*ie*, inorganic hydroxylated nanoscopic fluorides) able to produce such valuable compounds with unexpected high selectivity and productivity.

But not only the unacceptable high level of wastes and pollution is the nowadays problem of the humanity. The important reduction of fossil fuel reserves on which is based the current world economy corroborated with the global pollution and climate change is a major political, economic and scientific concern. To survive, our civilization has to make a strategically shift toward renewable fuels/products obtained *via* sustainable processes. In this context, the discovery and development of novel and efficient pathways for the conversion of the valuable bio-polymers (i.e., cellulose, hemicellulose and lignin) into bio-chemicals (also named "platform molecules") are among the big challenges facing heterogeneous catalysis.

In line with this nowadays challenge the development of efficient mono- and bifunctional heterogeneous catalysts and improving their efficiency and selectivity towards bio-chemicals as glucose, sweet alcohols, levulinic, lactic and succinic acid represent the

second important research direction which I approached in recent years and remain a prime objective for my future scientific development.

The successful use of the novel inorganic hydroxylated nanoscopic fluorides catalytic materials in the primary building block production from renewable resources is further evidence of their extraordinary catalytic capabilities. The scientific achievements in the development of these materials and their catalytic properties connected with the catalytic performances are discussed in detail in Section A, Chapter 1.

However, although the research in biomass valorization field is very intense and numerous novel transformation ways/catalytic materials were discovered in the last time, the specific properties of bio-polymers still impose new requirements on both processes and solids that are used as catalysts for their conversion. Therefore, despite of numerous solid acid catalytic systems applied in the aqueous phase hydrolysis of cellulose, the limited diffusivity of the feedstock, the low accessibility of the catalytic sites (related with a low catalytic activity), acidities that are difficult to adjust, or the lack of stability in the harsh used reaction conditions, are remaining problematic. The use of catalytic magnetic nanomaterials should overcome the problems connected to the low accessibility of the catalytic sites and the isolation and recovery from the reaction mixture of solid catalysts. Moreover, creating catalysts with multiple functionalities may bring the huge advances of direct transformation of cellulose into added value bio-chemicals. The research conducted in this area, developed in my group from University of Bucharest, lead to the development of magnetic nano-composites able to transform bio-polymers as cellulose directly to platform molecules, in a green manner. The most important scientific achievements in this area are discussed in Section A, Chapter 2.

Research in this field is very intense presently scientific worldwide and novel transformations and catalysts are being discovered at a high rate. Therefore, as I detailed in Section B, my future research career will continue on the broad fine chemistry and biomass valorization areas being optimistic that the knowledge acquired till now will allows me to create and develop novel catalytic systems able to offer even greater improvements in efficiency, selectivity, energy reduction, and rate enhancement in many chemical reactions. Since the accumulated experience in university education strongly convinced me that a modern research can not exist without a modern educational process just as university educational process can not exist without academic research, students will continue to be actively involved in this research by including them in the teams of my research projects and

supervising them in the elaboration of license, dissertation, and, after I receive the Habilitation certificate, PhD thesis on subject.

REZUMAT

Teza de Abilitare prezinta cele mai importante realizari stiintifice in sinteze de chimicale fine si valorificarea biomasei, obtinute dupa sustinerea tezei de doctorat, in 2001.

In mod cert Cataliza este un pilon fundamental al Chimiei Verzi si va continua sa fie principala forta motrice care va plasa intreprinderile chimice intr-un viitor durabil. Pentru aceasta, productia de chimicale, la ora actuala bazata pe cataliza (circa 90% dintre chimicale sunt produse pe cai catalitice), ar trebui deplasata din domeniul catalizei omogene in cel al catalizei heterogene (daca este posibil) pentru a evita contaminarea produsilor de reactie, reduce costurile de procese, intensifica recuperarea si favoriza reciclarea catalizatorilor. Astfel, in dorinta de a imbunatati procese industriale depasite sau de a initia noi procese de actualitate, intr-o maniera verde, s-au creat si dezvoltat noi catalizatori solizi eficienti si selectivi.

Sintezele de chimicale fine discutate s-au selectat dintre cele care inca ridica probleme de mediu la nivel industrial prin deseurile generate si consumul energetic ridicat, precum sinteza de vitamina E si K si sinteza de mentol. Cea mai importanta parte a acestei directii de cercetare, realizata ca bursier Alexander von Humboldt, sub indrumarea Prof. Erhard Kemnitz, la Universitatea Humboldt din Berlin, si mai apoi, dupa intoarcerea in tara, la Universitatea din Bucuresti, a condus la descoperirea unei noi clase de catalizatori (fluoruri anorganice hidroxilate nanoscopice) capabile sa produca astfel de compusi valorosi cu o selectivitate si productivitate neasteptat de ridicata.

Din pacate, nu doar nivelul inacceptabil de ridicat de deseuri si poluanti este problema actuala cu care se confrunta omenirea. Reducerea masiva a rezervelor de combustibili fosili pe care, la ora actuala, se bazeaza economia mondiala, alaturi de poluarea globala si schimbarile climaterice reprezinta o ingrijorarea majora la nivel politic, economic si stiintific. Pentru a supravietui, civilizatia noastra trebuie sa se deplaseze strategic catre combustibili/produsi obtinuti prin procese durabile. In acest context, descoperirea si dezvoltarea unor cai noi si eficiente de transformare a bio-polimerilor naturali (celuloza, hemiceluloza si lignina) in bio-chimicale (denumite si "molecule platforma") reprezinta una dintre cele mai mari provocari ale catalizei heterogena actuale.

In acord cu aceasta provocare, dezvoltarea unor catalizatori solizi performanti, mono- si bifunctionali, si imbunatatirea eficientei si selectivitatii acestora la bio-chimicale precum glucoza, alcooli dulci, acid levulinic, lactic si succinic reprezinta cea de-a doua directie

principala de cercetare pe care am abordat-o in ultimii ani si care va ramane un prim obiectiv pentru viitoarea mea dezvoltare stiintifica.

Utilizarea cu succes a fluorurilor anorganice nanoscopice ca si catalizatori in producerea de unitati primare de constructie moleculara (molecule platforma) din resurse regenerabile este o dovada in plus a capacitatilor catalitice extraordinare pe care acestea le poseda. Realizarile stiintifice in dezvoltarea acestor materiale si proprietatile lor catalitice in conexiune cu performantele lor catalitice sunt discutate in detaliu in Sectiunea A, Capitolul 1.

Totusi, desi cercetarea in domeniul valorificarii biomasei este foarte intensa, in ultimii ani descoperindu-se numeroase cai de transformare/materiale catalitice noi, proprietatile specifice ale bio-polimerilor inca impun noi cerinte atat proceselor cat si solidelor utilizate ca si catalizatori pentru transformarea lor. Astfel, in ciuda numeroaselor sisteme catalitice cu proprietati acide, aplicate in hidroliza celulozei, in faza apoasa, transportul de masa limitat al materiei prime, accesul limitat la centrii catalitic activi (corelat cu activitatea catalitica coborata), aciditatea dificil de ajustat sau lipsa stabilitatii in conditiile de reactie dure utilizate inca raman problematice. Utilizarea nanomaterialelor magnetice catalitice ar trebui sa preintampine problemele legate de accesibilitatea scazuta a centrilor catalitici dar si separarea si recuperarea catalizatorilor solizi din mediul de reactie. Mai mult, crearea catalizatorilor cu functionalitati multiple poate atrage dupa sine avantajul imens de a transforma celuloza direct in bio-chimicale, necesare productiei de compusi cu valoare adaugata. Cercetarea realizata in acest domeniu, in grupul de cataliza de la Universitatea din Bucuresti, a condus la dezvoltarea nano-compozitelor magnetice capabile sa transforme bio-polimeri precum celuloza si amidonul direct in molecule platforma, intr-o maniera verde. Cele mai importante realizari stiintifice in acest domeniu sunt discutate in Sectiunea A, Capitolul 2.

Cercetarea in acest domeniu este intensa, in cercetarea globala actuala, noi transformari si noi catalizatori descoperindu-se cu o frecventa uimitoare. Astfel, asa cum am detaliat in Sectiunea B, cariera mea stiintifica viitoare se va axa pe acest domeniu, cel putin in parte, dar va continua si pe problematica sintezelor organice fine, fiind optimista ca experienta deja acumulala in aceste domenii ma va ajuta sa creez si sa dezvolt noi sisteme catalitice, capabile sa ofere imbunatatiri chiar mai mari decat cele dezvoltate deja, prin eficienta, selectivitate, energetica si viteza de reactie intr-o gama larga de sinteze chimice importante la nivel aplicativ. Deoarece am convingerea, demonstrata de experienta acumulata in invatamantul superior, ca o cercetare moderna nu poate exista fara un proces educational modern la fel cum un proces educational universitar nu poate exista fara cercetarea academica, voi continua sa implic activ studenti in aceste domenii de cercetare prin

includerea lor in echipele de cercetare ale proiectelor pe care le manageriez si prin indrumarea acestora in realizarea lucrarilor de licenta, disertatie si, dupa primirea atestatului de abilitare, a tezelor de doctorat in subiect.