

Environmental & Green Chemistry 2017



5th International Conference on

Green Chemistry and Technology

&

6th International Conference on

Environmental Chemistry and Engineering

July 24-26, 2017 Rome, Italy

Keynote Forum Day 1

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Rajender S Varma, Trends in Green chem, 3:2
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Rajender S Varma

Palacky University, Czech Republic and Cincinnati, USA

Greener strategies for organics and nanomaterials: Sustainable applications of magnetic nanocatalysts and modified graphitic carbon nitrides

Sustainable efforts for the greener synthesis of diverse nanoparticles and their varied applications as recyclable and reusable nano-catalysts are important in this burgeoning field. Vitamins B1, B2, C, beet juice, antioxidants from blackberry, blueberry, pomegranate, turmeric and tea- and wine polyphenols, provide simple approach to bulk quantities of nanomaterials in eco-friendly medium. Synthesis via microwave (MW)-assisted spontaneous reduction of noble metal salts with sugars, MW cross-linking reaction of poly (vinyl alcohol) (PVA) with metallic systems and CNT's, formation of biodegradable cellulose composite films with noble metals; and the shape-controlled bulk synthesis of Ag and Fe nanorods in PEG will be depicted. MW process delivers magnetic nanoferrites and micro-pine structured catalysts from common metal salts. Sustainable route to nanoparticles using waste from winery or biodiesel byproduct, glycerol and their applications in catalysis (magnetic nanocatalysts or organocatalysis), toxicity and environmental remediation will be highlighted, especially their recyclability and reuse via magnetic separation. The utility of nano-catalysts (Pd, Ni, Ru, Ce, Cu, etc.) immobilized on biodegradable and recyclable supports e.g. cellulose and chitosan or on magnetic ferrites via ligands such as dopamine or glutathione will be presented. The utility of heterogenized bimetallic Ag-Pd nanoparticles on graphitic carbon nitride (AgPd@g-C₃N₄) will be highlighted and exemplified by upgrading of biofuel via hydrodeoxygenation of vanillin under visible light irradiation using formic acid as a hydrogen source including direct aminoforylation of nitroarenes. Photocatalytic C-H activation using VO@g-C₃N₄ catalyst for direct oxidative esterification of alcohols, oxygen insertion reaction in hydrocarbons and selective oxidation of alcohols and hydrogenation of alkenes and alkynes using visible light as the source of energy will be described; these strategies fulfill most of green chemistry principles whilst producing functional chemicals with extreme level of waste minimization.

Biography

Rajender S Varma completed his PhD from Delhi University in 1976. After Postdoctoral Research at Robert Robinson Laboratories, Liverpool, UK, he was a faculty at Baylor College of Medicine and Sam Houston State University. He joined Sustainable Technology Division at US EPA in 1999 and Palacky University, Czech Republic during the year 2014. He has over 40 years of research experience in management of multi-disciplinary technical programs and is extensively involved in sustainable aspects of chemistry that includes, development of environmentally benign methods using alternate energy input using microwaves, ultrasound and mechanochemistry and efficient technologies for the sustainable remediation of contaminants, and environmental sciences. Lately, he focused on greener approaches to assembly of nanomaterials and sustainable synthetic applications of magnetically retrievable nano-catalysts in benign media. He is a member of the Editorial Advisory Board of several international journals and has published over 455 scientific papers and awarded 15 US patents.

Varma.Rajender@epa.gov
rajvarma@hotmail.com

Notes:



Arthur Ragauskas

The University of Tennessee, USA

Valorizing lignin

The advent of commercial cellulosic ethanol production facilities globally, has brought to the forefront the need to address lignin valorization technologies. (1) Historically, the kraft pulp and paper industry addressed lignin generation issues by developing advanced combustion technologies to recover energy and cooking chemicals. But even this industry has begun to implement lignin recovery technologies and examine the use of lignin for material and chemical applications. (2) In the biofuel industry, lignin represents ~15-30% of the starting material and currently the only practical solution is combustion and yet this provides limited value while incurring high capital costs. Since lignin, is nature's primary polyaromatic bioresource it is clear that better solutions are needed. The historical challenges to utilization of lignin are several folds including variation of structure due to feedstock, broad variations in molecular weight and functionality and alterations in structure due to process isolation technologies. Currently, several of these are now being resolved, analytical advances facilitate precise determination of structure, lignin fractionation technologies provide control of the structure of lignin and novel catalytic conversion methodologies are being developed. (3) Our research studies have identified fractionation/pretreatments that predispose lignin for oleaginous organisms that utilize lignin to biosynthesize lipids which are a natural resource for biodiesel. (4) Likewise, lignin can be used for material applications and one of the promising routes is for green insulation as a lignin-based polyurethane foam. In this presentation we will examine these two conversion technologies and how they complement each other and how advances in lignin analytical chemistry help guide our conversion chemistry.

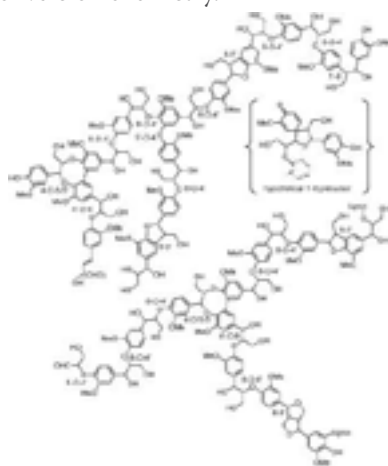


Figure 1: Native Softwood Lignin

Biography

Arthur Ragauskas held the first Fulbright Chair in Alternative Energy and is a Fellow of American Association for the Advancement of Science, the International Academy of Wood Science and TAPPI. In 2014, he assumed a Governor's Chair for Biorefining based in University of Tennessee's Department of Chemical and Biomolecular Engineering, with a complementary appointment in the UT Institute of Agriculture's Department of Forestry, Wildlife, and Fisheries. He serves in the US Energy and Environmental Sciences Directorate, Biosciences Division, at ORNL. His research program is directed at understanding and exploiting innovative sustainable bioresources. This multifaceted program is targeted to develop new and improved applications for nature's premiere renewable biopolymers for biofuels, biopower, and bio-based materials and chemicals.

aragausk@utk.edu

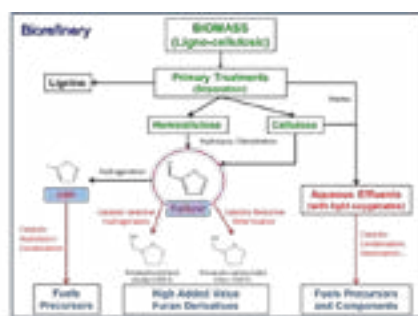


Marcelo E Domine

Instituto de Tecnología Química (UPV - CSIC), Spain

Novel heterogeneous catalysts and processes for biomass derivatives transformations into fuels and chemicals

A wide range of renewable raw materials and products can be easily obtained from ligno-cellulosic biomass and their derivatives in both polymeric (i.e. cellulose, starch, lignin) and monomeric (i.e. sugars, polyols, phenols) forms. These bio-based platform compounds could be converted into a large variety of chemical products and fuels to replace non-renewable fossil raw materials. The attainment of these bio-products is environmentally more favorable than that of their petroleum derived analogues, but also more expensive due to the lack of simple and efficient synthesis processes. In this sense, it is necessary to develop new highly selective catalytic processes allowing obtaining these bio-products in a competitive way (with lower energy consumption and higher profits) compared to conventional petro-products. Aligned with the new bio-economy and zero-waste concepts, the new bio-refineries should produce these bio-products for fuels and chemicals applications by reducing wastes, this includes both decreasing of side-products formation and residual effluents valorization in an integrated approach. In this presentation, the application of novel solid catalysts (with well controlled acid/base and redox properties) recently developed at ITQ for the efficient transformation of biomass derivatives into high added value products will be assessed. Particularly, catalytic processes for the production of chemicals starting from furfural will be discussed, such as i) the selective hydrogenation of furfural to tetrahydrofurfuryl alcohol, and ii) the reductive etherification of furfural to tetrahydrofurfuryl alkyl-ethers. In addition, solid catalysts will be evaluated in the production of precursors and components for fuels, such as iii) the hydrolysis/condensation of 2-methyl-furan, and iv) the valorization of oxygenated compounds present in biomass-derived aqueous fractions via ketonization/condensation, among others.



Scheme 1: Ligno-cellulosic biomass transformation in integrated biorefinery approach for fuels and furan derivatives co-production (Catalytic processes to be discussed in this presentation in red)

Biography

Marcelo E Domine completed his PhD at the Polytechnic University of Valencia (Spain) in 2003 under the guidance of Prof. A Corma, and Postdoctoral Studies at the IRCE-LYON - CNRS (France, 2005-07). In 2008, he re-joined the Instituto de Tecnología Química (UPV-CSIC) of Valencia, Spain as Scientific Researcher of CSIC. His current research involves the synthesis and characterization of solid catalysts and their application in sustainable chemical processes, mainly focusing on new biomass-derivatives transformations and wastes valorization into fuels and valuable chemicals. He is co-author of more than 55 publications (also including several patent applications). He has presented at over 18 invited conferences around the world. He has acted as Guest Managing Editor of *Catalysis Today*, and also as Reviewer in many renowned scientific journals in catalysis and fuels areas. He is actually the representative of CSIC (Spain) at the EERA Program – JP-Bioenergy (European Commission).

mdomine@itq.upv.es



Ioannis V Yentekakis

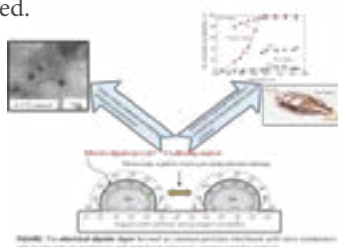
Technical University of Crete, Greece

Ionic conducting materials as effective catalyst supports with potential implementations in emissions control catalysis

Statement of the Problem: Nowadays, the abatement of CO, HCs, NO_x and N₂O emissions from automotive or stationary sources constitutes a subject of major environmental importance because of the major contribution of these pollutants to serious environmental problems, such as photochemical smog, acid rain, greenhouse effect and climate change as well as stratospheric ozone depletion (N₂O). Heterogeneous catalysis plays a key role in pollutant abatement technologies and often provides the most attractive and efficient solutions as, for example, in automotive emissions control – the most significant source of atmospheric pollution over the world. However, atmospheric pollution remains a huge and growing problem; therefore, an imperative need of even more efficient and economic catalytic abatement technologies remains as a highly desirable goal. An advanced catalyst promotion method that provides catalytic systems with exceptional activity and stability has currently attracted extensive attention for a wide range of applications related to energy production and environmental protection, is the subject herein.

Methodology & Theoretical Orientation: Ionic conducting materials as catalyst supports can be used as tunable metal-support interaction carriers, effectively controlling catalytic properties, via an effective dipolar layer of ionic promoter species formed at the catalyst particle surfaces, with concomitant dramatic effects on catalytic performance. The dipolar layer and its intensity (promoter species population), can be electrochemically controlled (Electrochemical Promotion or NEMCA effect) or can spontaneously be created on traditional-type highly dispersed catalysts, via thermally-driven spillover of ionic species from the support on the nanoparticle surfaces.

Conclusion & Significance: Worth noting achievements on environmentally important catalytic reactions (CO, HCs, NO_x, N₂O abatement) have been accomplished by this concept of promotion. An additional implementation of the concept, which concerns catalyst nanoparticles stabilization against thermal sintering, a subject of great importance in industrial heterogeneous catalytic processes, has recently been discovered.



Biography

Ioannis V Yentekakis is Full Professor of Physical Chemistry and Catalysis in the School of Environmental Engineering, Technical University of Crete (TUC), Greece. He received Chemical Engineering Diploma (1983) and PhD (1988) from the University of Patras. He has joined Princeton University USA, ICE-HT/FORTH Patras GR, Cambridge University UK as Senior Researcher, University of Patras, Dept. Chemical Engineering, as Assistant Professor (1996-2000), and finally Technical University of Crete as Associate (2001-06) and Full Professor (2006-today). He is regular member of the University Council of Technical University of Crete and Director of the Laboratory of Physical Chemistry & Chemical Processes. His current interest concerns development of novel materials and processes in heterogeneous catalysis for green and fine chemistry, environmental protection and renewable/sustainable energy generation. He authorized >100 peer-reviewed journal publications (with >3000 citations, h-index=32), >120 conference proceedings, 3 patents and 10 books.

yyentek@isc.tuc.gr

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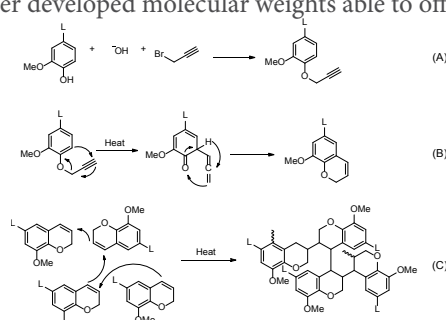


Dimitris S Argyropoulos

North Carolina State University, USA

Towards carbon fibers from single component kraft lignin systems: An application of green chemistry with forest biomaterials

Carbon fibers represent a class of materials with enormous potential for many materials and other engineering applications for our society. There are projections that by 2020 the actual demand for carbon fibers will be such that the traditional polyacrylonitrile precursors used today will not be enough to address the projected demand. Consequently, it is imperative that new precursors based on the foundations of green chemistry need be developed. In this respect, technical lignins present us with formidable challenges but also with enormous opportunities and they are to be explored in detail during this presentation. In our earlier effort, we have embarked in describing and discussing the importance of propargylation chemistry on lignin so as to synthesize lignin macromonomers for thermal polymerization via Claisen rearrangement. We have also discussed that the molecular weight and glass transition temperatures of the thermally polymerized lignin improves significantly relative to the starting material. The intricate polymer structure created within lignin as a result of the benzopyran double bond thermal polymerization chemistry is offering a regular covalently linked framework from which, after carbonization, a regular carbon fiber material could. As such, thermally polymerized propargylated softwood lignin emerges as a prospective material for the synthesis of bio-based carbon fiber precursor. Various reactivity considerations that are to be discussed in the presentation were addressed by a series of experiments where initially Acetone Soluble Kraft Lignin (ASKL) was propargylated, thus occupying all readily accessible and highly reactive phenolic-OHs, followed by methylation of the remaining phenolic OH's to limit phenoxy radical induced thermal polymerization. All the polymerization reactions were conducted by heating the samples at 180°C for three hours and the corresponding molecular weights and distributions were determined. As anticipated, the installation of the propargyl groups in more reactive positions, more readily prone to Claisen rearrangement and thermal polymerization events, offered much better developed molecular weights able to offer carbon fibers.



Scheme 1: The sequence of reactions that involves lignin propargylation (A) followed by Claisen rearrangement (B) and thermal polymerization (C)

Biography

Dimitris S Argyropoulos, Professor of Chemistry at North Carolina State University, is internationally recognized for his leading contributions to Green Chemistry using wood biopolymers. His work focuses on promoting our understanding of the structure and reactivity of lignin and the development of novel NMR and material science techniques for the structural elucidation and the upgrading of these biopolymers representing otherwise unsolved, intractable problems in lignin based material's chemistry. The efforts of his research group have been disseminated in excess of 200 scientific papers, numerous scientific conferences and invited presentations.

Dsargyro@ncsu.edu

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Sergiu M Gorun

Seton Hall University, USA

C-H free metal-organic green catalysts

The ultimate green catalyst for oxidations, molecular oxygen poses significant challenges when the catalyst contains C-H bonds. While enzymatic catalysis is a viable option *in vivo* since the biocatalysts are continuously regenerated, viable industrial processes using long-lasting, robust catalysts are preferred. Bioinspired catalysts that contain organic scaffolds related to hemes, but with all C-H bonds replaced by aromatic and aliphatic C-F bonds constitute a new class of materials that have been shown to perform chemical and photochemical aerobic oxidations and oxygenations of organic and biological substrates while resisting the reactive oxygen species they produce. This class of materials will be reviewed and its prospects in homogeneous and heterogeneous catalysis assessed.

Biography

Sergiu M Gorun has received his PhD from the Massachusetts Institute of Technology. Following an industrial career, he is currently Professor in the Department of Chemistry and Biochemistry at Seton Hall University in South Orange, New Jersey and the Director of its Center for Functional Materials.

sergiu.gorun@shu.com

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J Michael Köhler

Technical University of Ilmenau, Germany

Sustainable production means rational entropy management

The ways of production and consuming of energy are in the focus of public debate since decades. Energy is a key issue for industry, agriculture, traffic and everyday life. But, the reason behind the requirement of energy is the need of entropy production and entropy release. This fact concerns the management of energy as well as all use and conversion of materials. Not only all industrial processes include chemical and biotechnical synthesis, but also all other human activities are connected with the production and the transfer of entropy. The improvement of global entropy management is the most general challenge for realizing a sustainable working and living society. The urgent challenge for using renewable sources and of coupling agriculture with all other production chains is due to the fact that the area-related income of sun power and surface emission of infrared radiation is the global entropy export path of earth. Recent technical developments and challenges for future technology will be discussed in the frame of sustainable entropy export mechanisms.



Figure 1: The global energy flow and the global entropy export system

Biography

J Michael Köhler is the Head of the Department of Physical Chemistry and Microreaction Technology at the Technical University of Ilmenau (Germany) since 2001. He studied Chemistry in Halle an der Saale and Jena, where he also habilitated in General and Physical Chemistry (1992). He led a research department at the Institute of High Technologies in Jena between 1991 and 2001. During this time, he also taught at the Universities of Wuppertal and Jena. He *inter alia* has edited books on Microlithography, Micro System Technology and Nanotechnology. His current research interests are focussed on nanotechnology, on application of droplet-based microfluidics in nanoparticle syntheses and bioscreenings and on physicochemical aspects of sustainable chemistry.

michael.koehler@tu-ilmenau.de

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Ufuk Yildiz

Kocaeli University, Turkey

Novel macroporous cryogels with enhanced adsorption capability for the removal of Cu(II) ions from aqueous phase: Modeling, kinetics and recovery studies

Novel macroporous cryogels based on jeffamine with various molecular weights were prepared via freeze-drying method and then functionalized by successful reductive amination to yield reduced cryogels. The reduced cryogels were characterized by FT-IR and SEM and then used as adsorbents for removal of Cu(II) ions from aqueous solution. Preliminary adsorption test revealed that reduced cryogels showed 5 times higher adsorption capacity than non-reduced cryogels. Maximum adsorption capacities for Cu(II) ion removal were determined as 55.00, 46.73, 34.10 mg/g depending on the molecular weight of jeffamine used, at pH 5.5, temperature 55°C, dosage 80 mg and initial concentration of 100 ppm. Adsorption capacity of the reduced cryogels increases with increasing the initial concentration, pH, contact time and temperature but decreased with increasing adsorbent dosage. ΔH° values were calculated from the temperature dependence data and the obtained positive values indicated that the adsorption process was endothermic in nature. Performed recovery tests for the different cryogels resulted in a good response within the range of 56–70% recovery. The experimental adsorption data well fitted to Freundlich isotherm and pseudo-second-order kinetic model. The intra-particle diffusion and Boyd model confirmed that the adsorption process occurred via particle diffusion.

Biography

Ufuk Yildiz studied Chemistry at the Karadeniz Technical University and has done his PhD in 1998 supervised by Professor Baki Hazer. He joined at the Kocaeli University as an Assistant Professor in 1998. After his Post-doctoral work on miniemulsion and emulsion polymerization with Professor Markus Antonietti, Dr. Katharina Landfester and Dr. Klaus Tauer at Max Planck Institute of Colloids and Interfaces (Golm, Germany) he returned to Turkey and was promoted to an Associate Professor in the year 2004. He was a Visiting Scientist at the University of Liverpool, Department of Chemistry within the Centre for Materials Discovery working with Professor Andy Cooper and Dr. Jon Weaver (2008). He became a Full Professor in 2009. His research interests include macroinitiators, polymeric phthalocyanines, heavy metal ion adsorption, hydrogels and heterophase polymerization.

uyildiz@kocaeli.edu.tr

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