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Book Review

Producing Fuels and Fine Chemicals from Biomass Using Nanomaterials, by Rafael Luque and Alina Mariana Balu. CRC Press, Taylor and Francis Group, Boca Raton, FL 2014

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Reducing the dependence on the fossil fuels is of critical significance for continued economic growth and a better environment. Supplementing fossil fuels with renewable biomass is the first step to achieve this goal. Due to the element composition, almost all fuels and chemicals from petrochemistry can be generated from biomass by proper processes and catalysts, which motivates researchers to fill the gap in the area of design and development of nanomaterials for biomass conversion and utilization.

This comprehensive monograph covers the utilization of nanomaterials for biomass transformation to fuels, chemicals, materials as well as energy conversion and storage, practically the most important aspects from the design and development of nanomaterials to biofuels, biomass valorization, and solar cells. Chapter 1 is dedicated to *Introduction to Production of Valuable Compounds From Biomass and Waste Valorization Using Nanomaterials*. It is reinforced that why the theme covered in the book is important. The main context discussed in Chapters 2–11 is also briefly summarized.

The remaining chapters of the book constitute three sections. Section I—*Nanomaterials for Energy Storage and Conversion* follows a top–down structure, beginning with Chapter 2—*Green Carbon Nanomaterials: From Biomass to Carbon*—A general and indepth review is presented on production of green carbon materials prepared from renewable and highly abundant precursors, where the use and generation of polluting and toxic substances are avoided. These materials can be divided into two categories: crystalline (carbon nanotubes, graphenes, and graphene oxides) and amorphous (activated carbons, Starbons, and carbon materials from hydrothermal carboninzation). Both of them can be utilized for biofuel generation as heterogeneous catalysts. The author also highlights the numerous significant applications (e.g., hydrochar, adsorption, energy storage, and production) over Starbons and hydrothermal carbons, and indicates that hydrothermal carbonization is a simple and sustainable technique for generation of carbon materials, which can be easily integrated into future biorefineries. Carbon material is the most commonly used electrode material due to its unique properties (e.g., good electrical conductivity, relative low cost, high chemical resistance). The applications of energy conversion and storage over carbon materials are complemented and reinforced in Chapter 3—*Carbon Materials and Their Energy Conversion and Storage Applications*. The traditional carbon blacks and graphitic carbons could be improved in this field due to its uncontrollable microstructure and vulnerability to the electrochemical corrosion. Tailored novel nanomaterial-based carbon materials applied in a couple of applications such as fuel cells, solar cells, lithium-ion batteries, and electrochemical capacitors lead to improved performance compared with their counterparts in the corresponding applications, namely carbon nanomaterials and porous carbons with controllable pore structure. In Chapter 4—*Solar Energy Storage With Nanomaterials*—the utilization of metal oxide-based nanomaterials (binary and ternary metal oxides) in solar energy conversion and storage are focused. Metal oxides are widely studied due to their appropriate band gap, availability, and chemical stability. However, wide band gap of metal oxides limits their applications under the UV condition. Several approaches including dye sensitization, metal/nonmetal ion doping, the addition of solid solutions is employed to extend these oxides' application into the visible-light region. The crystallinity and size, in the design and development of an efficient photo catalyst for solar energy storage, also have a big impact.

In Sec. II—*Biofuels From Biomass Valorization Using Nanomaterials*—the importance of well-understood design and development of nanomaterials for biofuels generation is presented. The two most commonly used catalytic materials are supported noble-metals and transition-metal nanoparticles. Transition metals are less active and stable but much cheaper compared with noble metals in the dry reforming of biogas. Thus, the high cost limits their large-scale applications into biogas dry reforming. Chapter 5—*Catalytic Reforming of Biogas into Syngas Using Supported Noble-Metal and Transition-Metal Catalysts*—addresses these challenges (cost and carbon accumulation from CO disproportionation and methane dehydrogenation) in the dry reforming of biogas by several approaches toward the design of better transition metal catalysts, such as the promotion-by-poisoning of sulfur, metal doping to form bimetallic systems, and/or integration with supports that exhibits high oxygen mobility. Biodiesel is generated by transesterification over alkaline catalysts. However, the presence of free fatty acids (FFAs) higher than 0.5% in the feedstock hinders product separation. Neutralization is another concern. Therefore, solid acid catalysts are a good alternative to both alkaline catalysts and liquid acids in FFA esterification reactions. The commercial $Zr(SO_4)_2$ suffers from an unsatisfactory lifetime due to its partial solubility in water. Chapter 6—*Sulfated Inorganic Oxides for Methyl Esters Production: Traditional and Ultrasound-Assisted Techniques*—presents a very systematic study by tuning the properties of mixed-oxides via an ultrasound-assisted synthesis in a continuous or pulsed fashion. The best tuned sample with an enhanced acidity and a lower specific surface area is obtained with continuous ultrasound and higher powers. The presence of both Lewis and Brønsted acidity with

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acid sites mainly on the outer surface plays a major role for FFA esterification. The insight can be extended into other reactions such as alkylations, isomerizations, and esterifications of other carboxylic acids. Chapter 7—*Nanoheterogeneous Design of Biocatalysts for Biomass Valorization*—introduces final value-added chemicals from biomass by biocatalysis due to the excellent properties of biocatalysts (e.g., activity and selectivity) via two steps: biodegradation and biotransformation. However, naturally extracted enzymes are not suitable for industrial practice due to environment changes. Thus, improvement of the biocatalytic properties of the enzymes has to be performed. The authors highlight a covalent immobilization technique for the conversion of crude glycerol to biodiesel, bioethanol, and related high-added-value chemicals (1,3-dihydroxyacetone and glycerol carbonate), where biocatalysts are supported on nanoporous supports (e.g., functionalized magnetic Fe_3O_4 nanospheres coated with polymeric layers, core-shell Fe_3O_4–SiO_2, and carbon nanotubes). With a rational design, the combination of enzymes with magnetic nanoparticles shows a big advantage of a better separation of catalysts and activation of enzymes in the biomass valorization.

Section III—*Production of High–Added-Value Chemicals From Biomass Using Nanomaterials*—comprises the last four chapters, covering a design of nanostructured solid acidic catalyst and supported metal catalysts for the conversion of a wide range of starting biomass materials toward platform chemicals and end products. In Chapter 8—*Nanostructured Solid Catalysts in the Conversion of Cellulose and Cellulose-Derived Platform Chemicals*—Lignocellulose, as the major component of plant materials, can be converted into platform chemicals with subsequent processing into value-added chemicals by heterogeneous catalysis. The first step can be achieved by hydrolysis over solid acids or hydrolytic hydrogenation/hydrogenolysis over bifunctional solid catalysts, while the second one can be obtained by either catalytic oxidation or reduction reactions over solid catalysts. To tackle the bottleneck of limited contact interface between the solid catalysts and solid substrate, the context details the design of nanostructured solid acidic catalysts including transition metal oxides, zeolites, acidic-ion-exchanged resins, magnetic functionalized sulfonated silica, silica–carbon composites, sulfonated carbon materials for this initial step. The authors provide a general overview of oxidation and reduction of HMF and furfural over developed solid supported metal catalysts (support effect, particle size effect, bimetallic catalysts, etc.) for the production of value-added products from platform chemicals. Chapter 9—*Chemocatalytic Processes for the Production of Bio-Based Chemicals From Carbohydrates*—focuses on the industrial practice for carbohydrates transformation to many value-added chemicals, including furfural production from oat husks by Quaker Oats Co., 2,5-furandicarboxylic acid from hydroxymethylfurfural (HMF)/5-methoxymethylfurfural (MMF) by Avantium chemicals, p-xylene from glucose by GEVO, hydrocarbons from a glucose/xylose 97/3 mixture using BioForming process by Virent, aromatics from pure glucose by Annellotech, ethylene and glycols from glucose by Braskem, and isosorbide from sorbitol by Roquette. Due to the significant loss of mass during oxygen elimination in carbohydrate conversion, product yield is relatively low. The catalysts other than commercial ones discussed in this chapter show a higher selectivity/yield toward the desired products, indicating a rational design of heterogeneous catalysts could be a driver for the economic production of bio-based chemicals. *Synthesis of Fine Chemicals Using Catalytic Nanomaterials: Structure Sensitivity* is presented in Chapter 10. Particle size is found to have a profound effect on activity, selectivity and stability in structure sensitivity reactions. In continuation with biomass valorization, two case studies are presented and the concept is illustrated: isomerization of α-pinene to camphene and hydrogenation of thymol to methanol. Such an insight can be extended into structure sensitive chemistries of other case studies during biomass valorization. The Last Chapter—*Tunable Biomass Transformations by Means of Photocatalytic Nanomaterials*—summarizes the application of nanosized TiO_2 synthesized by sol-gel method for biomass transformation via photocatalysis, with three examples on water splitting, photocatalytic reforming, and photocatalytic transformations of biomass into high-value chemicals (e.g., photocatalytic oxidation of glucose into glucaric acid and gluconic acid with minimal total mineralization toward CO_2 and H_2O; transformation of malic acid into formic acid, acetic acid, and oxalic acid). In order to design a highly active and selective TiO_2-based photocatalyst with better spectral sensitivity, a few strategies should be considered, such as noble cocatalyst addition, anatase–rutile phase junction formation, strong metal–support interaction effect, ultrasound assistance in the sol–gel method.

This monograph represents a valuable instrument for policy makers, industrial professionals, professors, instructors, engineers, chemists, and students who are involved in stimulating biomass valorization into fuels and chemicals using nanomaterials.