

Editorial

Solid Catalysts for the Upgrading of Renewable Sources

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The use of renewable resources as raw materials for the chemical industry is mandatory in the transition roadmap toward the Bioeconomy. However, this is a challenge for the setup of catalytic processes based on heterogeneous catalysts.

First of all, when using biorenewables (particularly sugars) as starting materials, the process has to be designed in the condensed phase, as these kinds of molecules have little-to-no volatility and water is the solvent of choice with most bio-based systems. Moreover, many reactions designed to produce chemicals will also create water. This is the case for both etherification and esterification, which are widely used to produce fuel components and additives. For these reasons, the hydrothermal stability of the catalyst is one of the main problems when dealing with renewables.

Another issue is due to the highly oxygenated nature of plant-derived raw materials and platform molecules. This makes oxygen removal reactions such as dehydration, hydrogenolysis, hydrogenation, decarbonylation, or decarboxylation almost ubiquitous in biomass valorization pathways. Therefore, there is a need for robust hydrogenation or hydrogen transfer catalysts and also water-resistant acidic catalysts, and possibly for bifunctional materials where different active sites are present.

These challenges will be addressed in this special issue of *Catalysts* through several examples. A review article focused on the state of the art in the liquid phase depolymerization of lignin via catalytic transfer hydrogenolysis/hydrogenation reactions will open this interesting and current collection of papers [1]. Lignin is one of main structural components of lignocellulosic materials, and is widely available as a by-product in the pulp and paper industry and in the process of second generation bioethanol production. It could be a source of very valuable aromatic compounds if an effective method of depolymerization was available. It should be remembered that a shortage of aromatics, which are among the main building blocks in the chemical industry, is expected due to the shift from conventional fossil fuels to shale oil. This makes alternative routes to aromatics of particular interest. The review will also discuss the effect of lignin origin, as it is known that there are significant differences between hardwood, softwood, and straw lignins. The hydrogenolysis of dimethyl adipate to 1,6-hexandiol and the hydrogenolysis of xylitol in water to ethylene glycol, propylene glycol, and glycerol are the subjects of two other papers [2,3]. In particular, the hydrothermal stability of the catalyst used in the latter reaction was studied and improved by decreasing the amounts of aggressive by-products. Transfer hydrogenation is also one of the steps involved in the one-pot conversion of ethyl levulinate into gamma-valerolactone (GVL) [4]. In this reaction, a solid catalyst with both acidic and basic sites showing high thermal and chemical stability was successfully used. GVL is one of the most promising platform molecules we can obtain from biomass, as it can be upgraded to various chemicals and fuels, such as polymers, fuel additives, and jet fuel.

A second review deals with a class of hybrid materials that can act as bifunctional catalysts in biomass conversion due to their particular structure, namely Metal Organic Framework (MOF) [5]. The structures of MOF show coordinatively unsaturated (open) sites, with Lewis acidity in inorganic

nodes (metal ions) of the networks. These Lewis acids are of paramount importance for cascade processes in catalytic biomass upgrades such as depolymerization, dehydration, and isomerization.

The third review paper deals with catalysis processes for the synthesis of terpene-derived amines. Besides cellulose, hemicellulose, lignin and vegetable oils, mono- and sesqui-terpenes are one of the major classes of chemicals we can obtain from biomass. They are the main constituents of turpentine, obtained through the distillation of resins from trees, particularly coniferous trees, but also of essential oils. They can be used as raw materials for the synthesis of several products, including fuels, fine chemicals, and agro-chemicals. Moreover, in the last years they have attracted considerable interest as renewable resources for rubber and polymerization chemistry. Particularly relevant reactions in the field of terpenes are C–N bond formation ones. The review [6] reports on different strategies, namely reductive amination of carbonylic terpenes, hydroaminomethylation, hydroamination of double C=C bonds, hydrogen-borrowing methodology for amination of alcohols, and C–H amination of terpenes. The following paper [7] deals with an imino-Diels Alder reaction allowing one to produce tricyclic octahydroacridines in one pot and one step, starting from citronellal and aromatic amines and using a clay as the catalyst. Finally, the preparation of bio-derived carbon-derived materials to be used as hydrothermally stable catalysts for biomass transformation will be considered.

The fourth review [8] will compare two main methods for biochar synthesis (namely conventional pyrolysis and hydrothermal carbonization (HTC)) and the features of biochar with respect to other carbonaceous materials. Moreover, it will describe char modification strategies and some applications in the field of biofuels. The last paper [9] will describe a particular method to obtain a carbon-based material from sugars and taurine, allowing one to directly introduce strongly acidic groups on the surface.

This collection shows how numerous and multifaceted the research topics related to the exploitation of biomass are. Not only should catalysts comply with some particular stability requirements, but many processes should be re-thought to face the challenges of a new raw materials pool.

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