

Editorial

Catalytic Transformation of Lignocellulosic Platform Chemicals

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In the last years, renewable lignocellulosic biomass has attracted enormous interest due to the decrease of fossil resources and the progressive deprivation of the environment. In fact, biomass has emerged as a potentially inexhaustible resource for the catalytic conversion to chemicals, energy, and transportation fuels [1]. Strategic platform chemicals can be obtained as primary products directly from biomass conversion. Among them, levulinic acid (LA) represents a versatile bioproduct and one of the United States Department of Energy's (DOE's) top 12 bioderived feedstocks [2]. Whilst the processes for the conversion of biomass to LA are well established, the production of secondary LA derivatives needs further improvement.

This Special Issue has investigated significant challenges of the ever-evolving field of heterogeneous catalysis for the selective production of "secondary" biomass derivatives.

Among the downstream "secondary" derivatives of LA, alkyl levulinates are of particular interest due to their extensive applications not only as chemical intermediates, but also as sustainable additives for gasoline and diesel fuels [3]. Alkyl levulinates can be obtained by esterification of LA with alcohols using mineral acids, but the substitution of homogeneous catalysts by heterogeneous catalysts is highly desirable to avoid corrosion and environmental problems. Up to now, most studies were focused on the synthesis of ethyl levulinate, while the heterogeneous catalysis for higher levulinates' synthesis still needs optimization. In this Issue, Yang et al. have optimized the esterification of LA with n-butanol to give the valuable biofuel n-butyl levulinate, employing as catalyst a novel sulfonated amorphous carbon prepared from incomplete carbonization of glucose. This bioderived system displayed in the esterification a much higher catalytic efficiency than traditional commercial systems such as sulfonated active carbon, HZSM-5, or Nafion-212 and showed high stability [4]. On the other hand, γ -valerolactone GVL, obtained from LA hydrogenation, is one of the most important secondary biomass products, being a renewable and safe-to-store potential biofuel, but also a valuable solvent and an intermediate for fine-chemicals synthesis [5]. Up to now, LA conversion into GVL has been generally investigated starting from solutions of commercial pure levulinic acid, but these results cannot be extrapolated to raw solutions obtained from the acid hydrolysis of lignocellulosic material, due to the presence of many potentially detrimental compounds, such as the acid catalyst, coproduced formic acid, and soluble contaminants derived from the other biomass fractions. Thus, the direct use of these cheap solutions deriving from acid hydrolysis can cause severe poisoning effects on the hydrogenation catalysts and this aspect needs further investigation. In this Issue, Rivas et al. investigated the cascade valorization of *Eucalyptus globulus* wood to GVL without intermediate levulinic acid purification [6]. The raw solutions deriving from the acid hydrothermal conversion were directly employed for GVL production by levulinic acid hydrogenation with a commercial 5% Ru/C catalyst. The negative effect of coproduced formic acid present in these crude solutions was evidenced and efficiently counteracted by allowing the preliminary thermal decomposition of formic acid itself, allowing to obtain appreciable yields of GVL.

Moreover, the possibility of upgrading LA and GVL into other added-value compounds, such as 2-MeTHF, represents a smart possibility. In fact, 2-MeTHF, which can be obtained by catalytic hydrogenation of GVL or directly of LA, is a versatile, nontoxic organic solvent and a valuable biofuel [7]. In particular, GVL hydrogenation represents a challenging reaction, owing to the high thermodynamic stability of the GVL ring. Licursi et al. studied a cascade strategy for the catalytic valorization of levulinic acid and GVL to 2-MeTHF or to monoalcohols 2-butanol and 2-pentanol, employing water as a green medium [8]. The appropriate tuning of the catalytic system/reaction conditions can address the process toward to the selective production of 2-MeTHF or of monoalcohols. The use of commercial Ru/C and Re/C, together with niobium phosphate as acid cocatalyst, allowed the selective hydrogenation of γ -valerolactone and levulinic acid to 2-MeTHF. On the contrary, the use of zeolite HY with Ru/C allowed the selective production of the monoalcohols with remarkable yields.

In conclusion, this Issue clearly shows the importance of the optimization of heterogeneous catalytic processes for biomass conversion to “secondary” valuable chemicals.

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