Euro Green Chemistry 2019- From lignocellulose to valuable aromatics and fuels-Zhuohua Sun-Universitat Politècnica de València

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Introduction:

Lignocellulose is not edible, renewable starting material consisting of lignin, cellulose and hemicellulose, which shows significant potential for the sustainable creation of chemicals and fuels. As of now, unlocking this potential require fundamentally Novel catalytic methods and innovative biorefinery approaches that are able to contain the structural difficulty of lignocelluloses and derive value from all its major components. In a difficulty biorefinery, lignocellulose is first alienated to its constituents by pre-treatment. This method, however, is energy rigorous and predominantly focuses on producing high-quality cellulose. Moreover, under these method conditions the lignin contents are structurally modified, rendering its later catalytic valorization great challenging. This remains true despite impressive advances in the choosy conversion of lignin model compounds and depolymerization of organosolve lignin. In recent times, great research has focused on lignocellulose fractionation in the presence of catalysts. While these processes hold good promise for the good production of aromatic monomers from the lignin fraction, they leave a significant portion of the renewable carbon Equivalents unutilized and mixed with the catalyst. Thus, in these methods it is the cellulose part that is tedious to valorize and catalyst recycling has been identified as a key challenge. To allow efficiently catalyst recycling and get the valorization of all lignocellulose constituent without pretreatment, we devised methods that take benefits of the special reactivity of a copper doped porous metal-oxide catalyst in supercritical methanol. When these non-noble-metal catalyst was applied in a two-step manner during catalytic lignocellulose fractionation, the lignin content was transformed to aromatics in good selectivity, and the cellulose rich solid residues were totally altered to aliphatic small molecules, cathartic the catalyst for recycle and offering a distinct advantage over existing systems.

Significantly, this method deliver aromatic and aliphatic alcohols from lignocellulose, which maintain part of the functionality intrinsic to the renewable initial material and are thus preferably suited substrates for accomplishing direct, auto economic changes toward products with real valorization potential. Particularly, among these pathways are systematic ideas to get lignin-derived amines, including the high difficult direct coupling with ammonia, producing water as the only by-product. In general strategy seeks to get sustainability in the individual reaction steps and globally through reducing the number of reaction methods required and considerably falling the amount of waste formed. The selective balance between splitting and coupling pathways allows access to chemical diversity in products, which is necessary to get competitiveness with current fossil-fuel-based pathways.

Results:

The global catalytic plan established here consists of three stages in which lignocellulose are completely converted, giving a range of valuable products without any energy rigorous pretreatment. At the core of this method is the flexible use of a non-fine metal catalyst, copper dopped porous metal oxide (Cu_2O-PMO), in two different steps of this lignocellulose conversion process. Through mild reductive treatment an aromatic alcohol is obtain with high selectivity. Next, all process residue containing unreacted cellulose and lignin are fully converted to aliphatic low molecules, taking advantage of the sole reactivity of the Cu_2O-PMO in supercritical methanol. Therefore, the catalyst can be readily recycled. An advanced network of modifications was designed for the catalytic alteration of the obtained alcohols. These include the different fictionalization of the lignin derived aromatic alcohol to a minute library of value added compounds that can serve as pharmaceutical polymer building blocks. Focus is devoted to uncomplicated and atom economic methods that permit quick conversion of the Lignin derived platform chemical to good value yield that can enter the chemical supply chain at a much later on stage than bulk chemicals derived from petroleum. Secondly, convergent catalytic change of complex mixtures of cellulose-derived aliphatic alcohols to fuel-range alkanes via chain elongation and hydrodeoxygenation results in clean mixtures of alkanes. These methods are described in fully in the suitable sections of the manuscript. The flexible usage of Cu_2O-PMO for full material utilization. After getting 1G from pine lignocellulose in superb selectivity, the generality of the method was confirmed using a diversity of wood types recycle was included. Good aromatic monomer products were got in most cases, especially with poplar (36%), beech (31%) and maple (30%) lignocellulose. Fascinatingly, all product mixtures contained typically two, and a maximum of three products, the type of which depended on the subject structure of each lignin. We found alcohol 1S as the main product when starting from poplar, beech or maple lignocellulose.

Conclusions:

The catalytic methods developed here derive low value from both the lignin as well as the cellulose components of lignocellulosic biomass. The total technique embraces the difficulty of the renewable starting material and provides aromatic and aliphatic alcohol intermediates for additional direct transformations. This little model biorefinery provides access to a sort of products with concrete valorization potential. We have shown that aromatic alcohol 1G, isolated as a lone component, can serve as a lignin-derived platform chemical as it was obtain in good selectivity and altered to higher value building blocks including amines. Particularly, among these transformations is the direct coupling of 1G with ammonia. In addition, we found that the sole reactivity of the noble metal free catalyst (Cu20-PMO) used in the first, mild depolymerization step, enables the conversion of procedure residue that would otherwise block the catalyst to aliphatic little molecules, thereby enabling catalyst recycling. Gratifyingly, the following catalytic upgrading of the complex aliphatic alcohol mixtures to alkanes via chain elongation and hydrogeoxygenation was achieved, using non-noble-metal catalysts.