An efficient catalytic process converts sugary biomass into a renewable feedstock for polymer production

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The environmental impact of synthesizing adipic acid, an important precursor of nylon polymers, can be dramatically reduced by a chemical technique developed by Yugen Zhang and co-workers from the A*STAR Institute of Bioengineering and Nanotechnology.

The researchers found that an oxygen–rhenium catalyst complex transforms bio-based compounds derived from straw waste and other agricultural material into adipic acid with higher yields and lower emissions than conventional processes.

Producing bulk chemicals from renewable sources is a key objective for manufacturers seeking to reduce their dependence on petroleum-based raw materials. However, typical compounds produced by biorefining are quite different from current feedstocks. Many are made up of oxygen-rich sugar rings—mixtures that are thermally unstable and difficult to manipulate into new molecules. Finding ways to catalytically remove oxygen atoms from sugars, sugar alcohols and sugar acids is a critical challenge, says Zhang.

Recently, chemists have begun using a reaction known as deoxydehydration (DODH) to realize this goal. This technique uses oxygen–rhenium catalysts to remove neighboring hydroxyl (OH) groups from a hydrocarbon starting material and convert it into a double-bonded alkene—a compound more amenable to synthetic processing. But, until now, only sugar alcohols with multiple OH groups have been successfully converted by DODH reactions.

Zhang and his team examined whether mucic acid, a molecule that can be synthesized in large quantities from galactose sugar rings, would respond to DODH techniques. They dissolved the mucic acid in boiling alcohol and then added a pinch of the special oxygen–rhenium catalyst. This reaction worked better than expected, stripping off the sugar acid's OH groups with almost perfect efficiency. Zhang notes that this high reactivity can be traced to the two terminal carboxylic acid groups that activate mucic acid's internal carbon–OH bonds.

After synthesizing the double-bonded muconic acid derivative, the researchers transformed it into adipic acid by using a platinum–carbon

catalyst to hydrogenate the alkene positions—a simple chemical trick with only negligible byproducts. Further experiments revealed that the two-step mucic-to-adipic-acid bioconversion could be carried out in a single reaction pot with an overall yield of 99 per cent—a significant boost over the 60 per cent yields that standard protocols give.

The catalytic route also eliminates the nitrous oxide pollutants commonly released when petrochemicals are turned into nylon. "This highly efficient and green route for bio-adipic acid production should help draw more academic and industrial efforts to renewable feedstocks," says Zhang.

More information: Li, X., Wu, D., Lu, T., Yi, G., Su, H. & Zhang, Y. "Highly efficient chemical process to convert mucic acid into adipic acid and DFT studies of the mechanism of the rhenium-catalyzed deoxydehydration." *Angewandte Chemie International Edition* 53, 4200–4204 (2014). dx.doi.org/10.1002/anie.201310991

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