Catalytic Valorization of 2-methyl furoate to Diacids or Dicarboxylates

Mingchun Ye
Advisors: Raul F. Lobo
Committee Members: Christopher J. Kloxin, Marat Orazov, Alan M. Allgeier and Hari B. Sunkara

The catalytic conversion of lignocellulosic biomass-derived materials to monomers is an important goal in light of the need for sustainable and environmentally benign technologies. The production of furfural, furoic acid and methyl furoate relies on mature processes; these species are, however, mono-functionalized and are difficult to employ directly for polymer manufacturing. The 5,5’-coupling of two C5 derivates is one of the feasible methods available to prepare di-functionalized species and here we exploit this catalytic technology to prepare ready-to-use monomers. In this thesis, the coupling of 2-methyl furoate, and following reactions to the coupling product were investigated.

The first part of this thesis centers on the aerobic oxidative homocoupling of 2-methyl furoate catalyzed by homogeneous palladium complexes. The reaction conditions and composition were analyzed and optimized, and acceptable yields, good selectivity and fast reaction rate were achieved. The reaction mechanism was identified as the so-call “bimetallic mechanism”. Results showed the catalyst can be reused. Product separation by crystallization was also demonstrated.

In the second part I investigated the Diels-Alder dehydration tandem reaction of ethene with the dimethyl bifuran dicarboxylate (the coupling product of methyl furoate) to dimethyl biphenyl dicarboxylate. Homogeneous metal triflates were found to be effective catalysts. The reaction on the 1st ring proceeded relatively fast and is highly selective, however it was found that the cycloaddition to the 2nd ring was much slower, presumably due to the steric and electronic effects. Decarboxylation was an important side reaction competing with the 2nd ring reaction, and resulted in reduction of the carbon balance. Still, the yield for the biphenyl dicarboxylate was compared of current production method from fossil-materials and this was accomplished using unactivated precursors.

The third part is the hydrogenation of the bifuran dicarboxylic acid (the hydrolysis product of dimethyl bifuran dicarboxylate) to form octahydrobifuran dicarboxylic acid. Identification and quantification methods via the use of LC-MS and qNMR were developed. High yield and selectivity were achieved in water (as solvent) at mild temperatures. The reaction, rather than the dissolution of the solid reactant, was identified as the RDS by kinetic experiments. Specifically, the adsorption or desorption to (from) the catalyst surface was presumed to be the RDS.

Lastly, I investigated the hydrogenolysis/deoxygenation of the octahydrobifuran dicarboxylic acid to form sebacic acid with molecular hydrogen and homogeneous hydrogen iodide (HI) catalyst. Identification and quantification by LC-MS and derivatization+GC methods were developed to quantify the products. After the reaction conditions were optimized, a moderate sebacic acid yield was achieved. The hydrogenolysis of the 1st ring proceed effiently, but
opening of the 2nd ring was much harder. It is proposed that the interaction between the iodine atom and the oxygen atom in iodo-intermediates prevented the 2nd ring hydrogenolysis.

Overall, the reaction of coupling of 2-methyl furoate, and following DA dehydration, hydrogenation and hydrodeoxygenation reactions to the product(s) were investigated. Dimethyl bifuran dicarboxylate, dimethyl biphenyl dicarboxylate, octahydrobifuran dicarboxylic acid, and sebacic acid were formed at acceptable to good yield. Reaction mechanisms were proposed and verified, and recommendations were made for future research and improvement.