Abstract

Current production of adipic acid (one of the most important monomer building blocks in the polymer industry) is based on the nearly 80-year-old oxidation process of cyclohexane, producing environmentally harmful NOx compounds. The aim of the presented doctoral dissertation was to develop a sustainable process for the production of bio-based adipic acid from cellulosic sources. This doctoral thesis is divided into two studies; hydrodeoxygenation of model compounds with one oxygen-containing functional group, followed by dehydroxylation of aldaric acids (mucic and glucaric acid) into the final product, adipic acid (or its esters).

Based on the hydrodeoxygenation (HDO) study of model compounds (hexanoic acid, 1-, 2- and 3-hexanol, 2- and 3-hexanone, hexanal, methyl hexanoate and dihexyl ether) carried out in a three-phase batch reactor and catalyzed via NiMo/γ-Al_2O_3 catalyst, a micro-kinetic mathematical model describing the phenomena in all three phases and on the catalyst surface was developed. In the second part, based on the developed mathematical model, initial assumptions were proposed for HDO of a more complex system, i.e. HDO of aldaric acid, which has free carboxylic groups at the terminal sites and one hydroxyl group on each intermediate C atom. In this experimental study, various reaction conditions and metal catalysts on different supports were tested for HDO of aqueous mucic acid. In aqueous media mucic acid readily forms a lactone while the tested catalysts showed negligible or too high (resulting in C-C bond cleavage) activity.

The final section was focused on selective removal of –OH groups from aldaric acids via homogeneous and heterogeneous Re catalysts on different supports. Presence of homogeneous catalysts resulted in successful removal of –OH groups as a 50 mol% yield of dehydroxylated products (with two, one or no double bonds) was obtained. The reduced Re/C catalyst proved to be the most effective as a yield of dehydroxylated products, obtained at 175 °C after 60 h of reaction in methanol as solvent, was 98 mol%, the highest published yield ever reported. The developed process was successfully described by the mathematical model, which included dissolution of aldaric acid, transport phenomena, adsorption, desorption, and kinetic reactions on the catalyst surface.

Keywords: Lignocellulosic biomass, aldaric acid, adipic acid, catalytic hydrodeoxygenation, dehydroxylation, mathematical modeling, reaction kinetics.