Formic and Levulinic Acid from Cellulose via Heterogeneous Catalysis

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Akademisk avhandling

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Abstract
The chemical industry of today is under increased pressure to develop novel green materials, biofuels as well as sustainable chemicals for the chemical industry. Indeed, the endeavour is to move towards more eco-friendly cost efficient production processes and technologies and chemical transformation of renewables has a central role considering the future sustainable supply of chemicals and energy needed for societies. In the Nordic countries, the importance of pulping and paper industry has been particularly pronounced and the declining European demand on these products as a result of our digitalizing world has forced the industry to look at alternative sources of revenue and profitability. In this thesis, the production of levulinic and formic acid from biomass and macromolecules has been studied. Further, the optimum reaction conditions as well as the influence of the catalyst and biomass type were also discussed. Nordic sulphite and sulphate (Kraft) cellulose originating from two Nordic pulp mills were used as raw materials in the catalytic one-pot synthesis of green platform chemicals, levulinic and formic acid, respectively. The catalyst of choice used in this study was a macro-porous, cationic ion-exchange resin, Amberlyst 70, for which the optimal reaction conditions leading to best yields were determined. The kinetic experiments were performed in a temperature range of 150–200 °C and an initial substrate concentration regime ranging from 0.7 to 6.0 wt %. It was concluded that the most important parameters in the one-pot hydrolysis of biomass were the reaction temperature, initial reactant concentration, acid type as well as the raw material applied. The reaction route includes dehydration of glucose to hydroxymethylfurfural as well as its further rehydration to formic and levulinic acids. The theoretical maximum yield can hardly be obtained due to formation of humins. For this system, maximum yields of 59 mol % and 68 mol % were obtained for formic and levulinic acid, respectively. The maximum yields were obtained in a straight-forward conversion system only containing cellulose, water and the heterogeneous catalyst. These yields were achieved at a reaction temperature of 180 °C and an initial cellulose intake of 0.7 wt % and belong to the upper range for solid catalysts so far presented in the literature. The reaction network of the various chemical species involved was investigated and a simple mechanistic approach involving first order reaction kinetics was developed. The concept introduces a one-pot procedure providing a feasible route to green platform chemicals obtained via conversion of coniferous soft wood pulp to levulinic and formic acids, respectively. The model was able to describe the behavior of the system in a satisfactory manner (degree of explanation 97.8 %). Since the solid catalyst proved to exhibit good mechanical strength under the experimental conditions applied here and a one-pot procedure providing a route to green platform chemicals was developed. A simplified reaction network of the various chemical species involved was investigated and a mechanistic approach involving first order reaction kinetics was developed.

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