Chapter 1

Overview

Catalysis plays a critical role in the production of commodity chemicals from crude oil. Heterogeneous catalysis is key to approximately 90% of such processes in the petroleum refinery. Biomass is expected to be a sustainable carbon source that can replace oil within the current refinery scheme. Several similarities can be drawn between the petrochemical processes and biofuel production. However, the great differences in composition between crude oil and biomass make utilization of biomass challenging. The high oxygen content leads to poor quality fuels and for this reason (hydro)-deoxygenation processes have to be applied. Deoxygenation of biomass can be achieved via hydrogenation and hydrodeoxygenation (HDO). In both circumstances, a hydrogenation catalyst is required in order to activate hydrogen, which is then added to the substrate. Raney Ni is an inexpensive skeletal metal catalyst. By using concentrate sodium hydroxide solutions, this heterogeneous catalyst is produced via the partial leaching of aluminum from an Ni-Al (1:1) alloy. Skeletal Ni catalysts have been employed for several types of reaction, including hydrogenation, transfer hydrogenation, hydrogenolysis, and dehydrogenation. In this thesis, Raney Ni is investigated as an H-transfer catalyst for hydrogenolysis and hydrodeoxygenation of lignin, which is one of the major components of
Overview

lignocellulosic biomass. The goal is selective deconstruction of lignin into intermediates for the production of value-added chemicals.

In Chapter Two, an introduction of biomass composition and structure is provided. The primary existing fractionation processes of lignocellulosic biomasses are succinctly reviewed. Furthermore, the state-of-the-art utilization of biomass-derived commodities and catalytic processes recently developed for the production of chemicals from lignin are introduced.

In Chapter Three, hydrogenolysis reactions of lignin are described. Raney Ni is selected as a hydrogenation, catalyst and molecular hydrogen (H₂) is added to the lignin structure in order to depolymerize lignin into corresponding monomers. Together with hydrogenolysis, which leads to the production of ortho-methoxyphenols, hydrogenation of the ring occurs and cyclohexanols are obtained. Lignin feedstocks were obtained from an organosolv process and from the mechanocatalytic depolymerization of wood.¹² A comparison of processes performed on these raw materials shows that the conversion is higher for the organosolv lignin compared to lignin obtained via the mechanical catalytic depolymerization of wood (MCP-L). The difference in reactivity may be related to the poor solubility of MCP-L in organic solvents (e.g. acetone). However, other factors may also influence the conversion of lignin (e.g. carbohydrate content and condensation).

In Chapter Four, the procedure for mechanical catalytic depolymerization of wood is improved. The saccharification step is performed in the presence of 2-methyl tetrahydrofuran (2-MeTHF) water mixture. Lignin is mostly extracted into the organic layer (2-MeTHF), whilst carbohydrates (e.g. cellulose and hemicellulose) are depolymerized into monomers and recovered in aqueous phase. The obtained lignin (E-L) exhibits high solubility in organic solvents and, therefore, higher reactivity than MCP-L. Moreover, hydrogenolysis reactions, performed in the presence of Raney Ni and H₂, leads selectively to ortho-methoxyphenols without saturation of the ring.
In Chapter Five, a low-temperature deoxygenation route, performed in the presence of Raney Ni and a solid acid catalyst, is applied to a variety of phenol in order to convert them into arenes. 2-Propanol (2-PrOH) is employed as the hydrogen source for the hydrogenation of phenol into cyclohexanol, which is dehydrated by the solid acid catalyst into cyclohexene. Raney Ni catalyzes the dehydrogenation of cyclohexene into benzene as a tandem process. The reaction conditions are optimized and applied to a lignin-derived bio-oil.

Finally, in Chapter Six, a new procedure for the selective conversion of phenol into arenes is described. Raney Ni alone catalyzes the selective conversion of phenol derivatives into arenes in the presence of alkanes, which can be also employed as a hydrogen source. The presence of a solvent with low basicity is strictly necessary for this reaction. Indeed, a solvent with high basicity (e.g. 2-PrOH, 2-MeTHF) could inhibit the Lewis acidic sites of Raney Ni and lead to hydrogenation of the ring. The stability of the catalyst is explored and enhanced by using stoichiometric quantities of alcohols. Furthermore, the reaction is successfully applied to the reaction of a lignin-derived bio-oil.