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Converting lignin to aromatics: step by step

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Chapter 2

Lignin and lignin-model compounds: catalytic depolymerization to aromatics

Abstract

Chapter 2 provides an overview of the catalytic depolymerization research using lignin or model compounds. Catalytic reduction and oxidation are presented, covering different studies from conventional catalysts to noble metal supported catalysts. The development and improvement of selective catalytic reactions, such as hydrodeoxygenation, are fundamental to enhance the catalytic valorisation of lignin towards high value aromatics including benzene, toluene and xylene (BTX) and phenols.

2.1. Introduction

The separation of biomass into distinct streams of hemicellulose, cellulose and lignin is no longer an obstacle for biorefineries. Hence, their valorisation to higher value chemicals has become a priority of biobased research. If hemicellulose and cellulose are used in several processes of value added applications, lignin is still considered as a waste. Therefore, the development and improvement of selective catalytic reaction are fundamental to enhance the depolymerisation of lignin towards high value aromatics, for example benzene, toluene and xylene (BTX) and phenols.

2.2. Catalytic reduction and hydrodeoxygenation

In petroleum refineries, hydrocracking is the process where the heavy hydrocarbons are fragmented into smaller alkanes, breaking C–C bonds. Fluid catalytic cracking is a succession of hydrogenation, hydrogenolysis, hydrodesulfurization and hydrodeoxygenation steps at elevated temperature and high hydrogen pressure.[1] The most commonly used catalysts are bifunctional catalysts, combining the activity of metals such platinum, palladium, molybdenum or nickel over a support of silica-alumina.[1] Similar catalysts and conditions have been studied in lignin depolymerization strategies as early as 1938.[2]

One of the first patented processes is the Noguchi process.[3] Different co-catalysts were tested such as copper, silver, tin, iron, cobalt, chromium, nickel, zinc and molybdenum at temperature between 250–450 °C and hydrogen pressure of 150–450 bar. Using an iron based catalyst (Fe–S–Cu–Sn ratio 10:12:1:1) in a batch reactor, the best yield of monophenol from lignin was 21%.[3] Urban et *al.* synthesized the catalyst *in situ* and improved the process affording, 45% of cresols and 65% of monophenols from kraft lignin.[4]

Liquification of lignin to aromatics uses xylenol as a liquid dispersing agent and ferrosulfate as a hydrogenation catalyst.[5] In this process, lignin is depolymerized under rush conditions and the distillable products obtained contain a substantial amount of

phenolic products.[5] Using only 2.5 wt% of catalyst, practically 100% of lignin is converted to about 60% in distillable aromatic products.

In 1987, UOP Inc. patented the hydrocracking of lignin to phenolic products using a supported tungsten-nickel catalyst, which affords high yield and great selectivity.[6] Under hydrogen atmosphere, tungsten oxide is reduced to its metal state. Therefore, the catalyst is more active in cracking than in hydrogenolysis of lignin. The advantage of this catalyst is its stability toward sulfur content feedstocks.

2.2.1. Conventional catalyst for hydrodeoxygenation: CoMo and NiMo

The most studied system though is a combination of the sulfided CoMo and NiMo catalysts over different supports. In 1983, a process combining hydrotreatment and thermal dealkylation was patented.[7] Using an ebullated-bed reactor, lignin was treated at 400 °C to produce, according to the findings, 37% yield of phenols based on the organic content of lignin. This process used an alumina supported iron or molybdenum catalyst promoted with cobalt or nickel.[7]

To understand the fundamentals of these catalysts, several studies were performed on monomeric model compounds having functional groups that mimick the original structure of lignin, such as cresol, anisole or guaiacol.[8-10] The deoxygenation mechanism over sulfided catalyst is commonly known to occur on the active sites situated on the sulfur vacancies present on the edges of the MoS_2 phase.[11] However, it is not clear yet how the promoting effect of nickel or cobalt is affecting the vacancies number or electron donating properties. Notably, when cobalt or nickel is used as copromoter, the activity of the catalyst is greatly increased.[11] NiMo promoted catalysts produce generally more hydrogenation (HYD) reaction, and hence CoMo supported catalyst are usually preferred when the aromaticity should be maintained. Some studies use sulfided $CoMo/Al_2O_3$ catalyst around 300 °C with 50 bar of hydrogen. In these cases, the main two reactions observed are demethylation and hydrodeoxygenation (HDO).[8, 9] It was observed that for the hydrodeoxygenation occurs at slower reaction rate compared to the demethylation reaction. The hydrodeoxygenation to benzene is the main reaction when phenol was chosen as a model compound, see Scheme 3.[9]
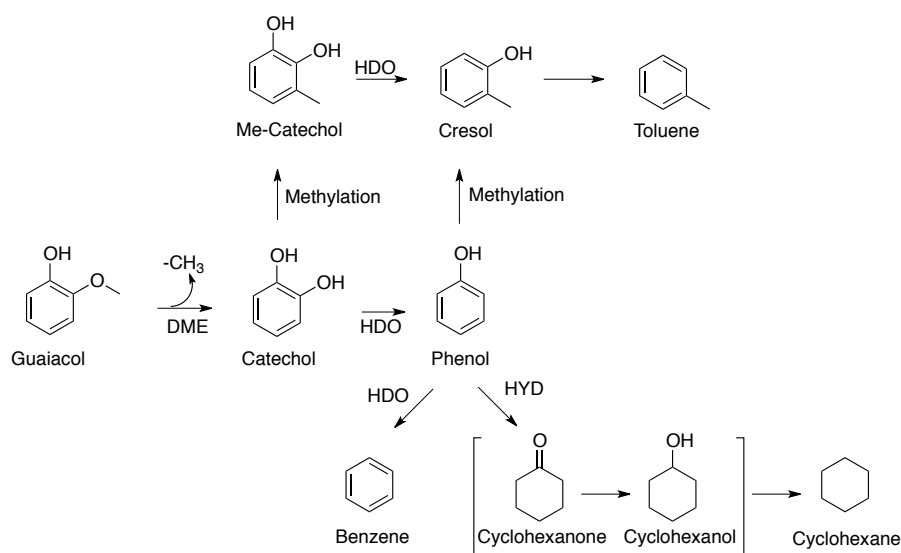
Scheme 3: Guaiacol observed pathways using sulfided CoMo catalysts.[9]

Bui *et al.* studied in detail the influence of the support by testing various oxides like Al_2O_3, ZrO_2 and TiO_2 on the conversion of guaiacol.[9] Sulfided CoMo supported on alumina and titania catalysts gave similar activities. The activity in HDO for the catalyst supported on ZrO_2 was much higher. Interestingly, the three supports promote different reaction pathways. When alumina supported catalysts are used, methylated compounds were the main reaction products.[9] For titania supported catalysts, the main product formed was methane, while using zirconia mostly methanol is obtained. The differences in activity to hydrodeoxygenation were attributed to the nature of the hydroxyl group where the adsorption takes place. The amphoteric nature of zirconia is essential in this case.[9]

Yet sulfided catalysts suffer from several drawbacks. The reduction of the sulfided Co and Ni to a zero-valent state, which is then followed by coke formation gives them poor life time stability and rapid deactivation.[12] As these catalysts are inspired from a high sulfur feedstock like crude oil, when used with biomass, the low sulfur contents make the catalysts unsuitable for large-scale applications.

2.2.2. Noble metal catalysts for hydrodeoxygenation

Noble metals have also been tested in the catalytic HDO of lignin and model compounds. In the late 60s, Pepper and Lee reported the depolymerization of lignin over different noble metal catalysts such as Raney Nickel, palladium, ruthenium and rhodium using carbon as support.[13] However, yields of phenols were rather low accounting for a maximum of 2.6 wt%. More recently, Liguri and Barth published an elegant process where lignin is depolymerized under hydrogen transfer using formic acid in the presence of Pd/C catalyst and Nafion (sulfonated tetrafluoroethylene).[14] Using water as solvent and at temperature of 300 °C, the final reaction mixture consisted of three phases. In the gas phase, the decomposition of formic acid was identified as well as gasification of lignin bridging groups. The catalyst and the unreacted lignin were in the solid phase and the liquid phase was a mixture of phenol derivatives mainly guaiacol, pyrocatechol and resorcinol. The percentage of the products varied depending on the source of lignin.[14]

Using guaiacol as model compound, high yields and selectivity to phenol were achieved with a PtSn bimetallic catalyst supported on an Inconel (trademark for a nickel/chromium support). Selectivity to phenol reached 80% and complete conversion of guaiacol is observed. Notably, the bimetallic catalyst deactivates to a far lower extent than its monometallic analogs.[15,16] The side products of the reaction are benzene and *o*-cresol. A carbon nanofiber (CNF)/Inconel support can improve the selectivity to benzene with the same yield of conversion. However, higher hydrogenation of the aromatic ring (to cyclohexanol, 2-methoxycyclohexanol, cyclohexane) occurs when using monometallic catalysts.

Lee *et al.* reported that for a given support, Pt, Rh, Pd, and Ru monometallic catalysts had similar product distributions.[17] At low reaction temperatures, hydrogenated products were observed. At temperatures higher than 250 °C, HDO was the main reaction.[17] Lin et al. compared the activity of a Rh-based and conventional sulfided catalysts for guaiacol reactions.[18] Their main finding was that the addition of Pt or Pd did not improve the activity or selectivity of Rh/ZrO$_2$ catalysts.[18] Below 400 °C, all Rh-based catalysts showed significantly increased activity compared to their sulfided CoMo

and NiMo analogs. Nevertheless, the Rh-based catalysts gave also hydrogenation of the aromatic ring.[18]

2.3. Catalytic oxidation

The principle of catalytic oxidation of lignin relies on increasing the oxygen functionality, mostly towards aldehydes incorporated into the aromatic products of lignin depolymerization.[19] At industrial scale, vanillin is produced via catalytic oxidation of alkaline lignin. Starting from lignosulfonates, lignin is oxidised under oxygen atmosphere at high pH, temperatures around 150 °C and 10 bar.[19] Several studies focused on the mechanistic pathways involved in the production of vanillin under those conditions.[20, 21] The following intermediate and compounds are proposed to be formed: phenoxyl radicals (by the detachment of one electron from phenoxyl anion), quinone methyde (by desproportionation of phenoxyl radical), formation of coniferyl alcohol (by nucleophilic addition of hydroxide ion), gamma-carbonyl (by oxidation of coniferyl alcohol) and vanillin (by the retro-aldol cleavage of the $\alpha-$ and $\beta-$unsaturated aldehydes).[20, 21] The use of catalysts such as cupric salts can double the production of vanillin.[21]

Noble metals can also be effective catalysts in the production of aldehydes from lignin.[22] In a batch slurry reactor operated in a continuous fluidized-bed reactor, lignin is oxidized by partial oxygen pressure of 5-10 bar and temperature of 100-120 °C over a palladium catalyst supported on alumina.[22] Scaling-up the reaction to a continuous process increases the aldehydes production considerably. The main products were aldehydes such as vanillin, syringaldehyde and *p*-hydroxybenzaldehyde.

Bhargava et *al*. investigated the role of copper catalysts on the degradation of ferrulic model compounds.[23] Several catalysts were tested among which metallic copper, bimetallic catalysts (Cu-Ni, Cu-Co and Cu-Mn), a mixture of reduced metals (Cu-Ni-Ce supported on alumina) and mixture of metal oxides (Cu-Ni-Mn and Cu-Ni-Fe).[23] Cu-Ni-Ce/Al_2O_3 was the most active catalyst but had the highest leaching of copper, where Cu-Mn/Al_2O_3 was the most stable catalyst tested.[23]

2.4. Motivation and aim of this work

Since 2000, a number of processes were patented on the transformation of cellulose and hemicellulose to more valuable chemicals. So far, there is still no viable process for converting lignin into high value added chemicals. Because of its complex and recalcitrant nature, selective depolymerization of lignin is a real challenge. The pulp and paper sector produces massive amounts of lignin by-product, currently burned as a fuel. Burning lignin is wasteful, because it is in fact the most abundant natural resource of aromatic compounds. Its selective depolymerization to platform chemicals like benzene, toluene and xylene (BTX) and phenol is much more attractive.

The main goal of this thesis was to target aromatic building–blocks such as (BTX) and phenol using heterogeneous catalysts. As lignin is typically over-functionalized, the main reactions encountered in lignin depolymerization are demethoxylation/demethylation and hydrodeoxygenation reactions. These reactions are hence explored in chapters 3, 4 and 5 using unconventional catalysts. Different monomeric and dimeric model compounds were selected, catalysts synthesized, characterized and screened to understand the fundamental factors governing these reactions.

Surface reactions of the adsorbed species are crucial to explain the selectivity of the hydrogenolysis of C–O bonds. In both demethylation and hydrodeoxygenation, choosing the appropriate active metal as well as the support can have a great influence. Acidic catalysts are known to increase adsorption of the substrates, but the addition of basic sites can enhance the selectivity toward the hydrogenolysis of the C–O bonds. Understanding the reactivity of the catalysts under the specific reaction conditions was a strong motivation in the work done in every chapter.

Finally, the challenge of developing new conditions to solubilize lignin without addition of alkaline salts encouraged us to build an entire set-up suitable for liquid ammonia. The building of the set-up is presented in an appendix describing every connection detail and sealing materials needed for the construction. The reactor was equipped with a glass window on each side, which allowed us to follow the

solubilisation process in time. Excitingly, liquid ammonia as solvent exhibits different properties than water and can interact with lignin in a gentle manner. Compared with water experiments, lignin can be fully solubilized in liquid ammonia at room temperature.

2.3. References

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