Sustainable pathways to chemicals and fuels from lignocellulose via catalytic cleavage and coupling reactions
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Summary and Outlook

This thesis described several developments on the use doped porous metal oxides as catalysts in the field of renewable resources. Strategies have been presented that open new, more efficient ways of lignocellulose utilization and conversion to value added chemicals and fuels. Different copper doped porous metal oxides (Cu-PMO) catalysts were used and modified for different catalytic processes. Two main catalytic strategies are applied as the core concept for this thesis based on either specific bond cleavage or bond formation reactions. Chapter 2 and 7 focused on the selective cleavage of C-O bonds in lignocellulose and other chapters describe the C-C and C-N bond formation strategies for upgrading lignocellulose derived chemicals.

Chapter 2 described a two-step lignocellulose conversion process (LignoFlex) using a Cu20-PMO catalyst. This process, which is inspired by the RCF process, demonstrated a novel solution for valorization of both lignin and (hemi)cellulose integrated with recycling of catalysts. In the first step, a single aromatic alcohol (4-propanolguaiacol, 1G) is obtained in excellent selectivity (>90%) by using pine lignocellulose. In the second step, the unreacted (cellulose rich) residues were able to be fully converted to aliphatic low-molecular weight alcohols in supercritical methanol, thereby liberating the catalyst for re-use and offering a distinct advantage over existing catalytic lignocellulose conversion strategies. Control reactions suggested that copper present in the catalyst and hydrogen gas are both important for this process. Mechanistic studies using synthetic lignin model compounds showed that Cu20-PMO catalyst had unique activity and selectivity for lignin depolymerization via cleavage of the most-abundant β-O-4 linkage. Catalyst recycling tests using pine lignocellulose showed a full lignocellulose conversion for a total of 10 runs (5 mild, 5 supercritical). This catalyst also performed a wide applicability for conversion of different feedstocks and a good correlation was also found between the syringyl/guaiacyl (S/G) ratio of native lignin and the corresponding aromatic monomer products.

In Chapter 3, the work of Chapter 2 is continued, which mainly focused on the obtained aromatic alcohols from step 1 of LignoFlex. As shown in Chapter 2, using LignoFlex both 1G (4-propanolguaiacol, 22 mg) as well as 1S (4-propanolsyringol, 31 mg) could be isolated as pure compounds from maple wood (1 g). These intermediates maintain important functionality that allows direct conversion to higher value products. Regarding lignin valorisation, such approach is a viable alternative to strategies that attempt to convert lignin into chemicals of very low functionality, in particular when products containing heteroatoms are desired. After screening several catalysts and reaction conditions, finally we established a direct transformation of 1G to corresponding nitrile (4-propanenitrileguaiacol, 4) with ammonia using a commercially available Ni/SiO2-Al2O3 is established. 4 was obtained in good yield (69%) and could be further converted to the corresponding amine or acid by application of simple hydrogenation or hydrolysis reactions. By using the same catalyst,
without adding ammonia, both 1G and 1S can be defunctionalized to 3G (4-ethylguaiacol) or 3S (4-ethylsyringol) with good selectivity. The potential applications of the obtained chemicals as pharmaceutical and polymer building blocks were then discussed in this Chapter. The established pathways show that the produced aromatic alcohols can serve as a lignin-derived platform chemical as they were obtained in high selectivity and can be converted to higher-value building blocks such as amines.

Chapter 4 focused on upgrading of alcohol mixtures (SMix) from the second step of LignoFlex described in Chapter 2 in order to obtain valuable fuels. The short chain length of single molecules of SMix was addressed by a two steps process; a chain elongation and a hydrodeoxygenation (HDO) reaction using non-noble-metal catalysts. Cyclopentanone which can be obtained from catalytic conversion of furfural is selected as the coupling partner for the chain elongation reactions. In consideration of the complexity of SMix, studies were first studied with simple model compounds. CuNi-PMO catalysts which also showed good activity in the Guerbet reaction with ethanol (Chapter 5) were found to be a good candidate for coupling alcohols with cyclopentanone. The obtained ketones could be converted to alkanes by a Ni/SiO$_2$-Al$_2$O$_3$ catalyst. After studies with model compounds, the real Lignoflex mixtures (SMix) were then tested. Overall, a good yield of alkanes (54%) was obtained using the developed two-step process. The components of the product mixture fell into two main categories: i) C4–C6 alkanes originating from branched or cyclic uncoupled alcohols; and ii) transportation fuel range, C8–C11 alkanes from the coupling of cyclopentanone with aliphatic alcohols and of lignin-derived propylcyclohexanols. However, in this process, not all alcohols are upgraded and leave a lot of short chain alcohols unreacted which end up to short chain alkanes after HDO reactions. Which means the catalytic system is still not efficient enough. Further research will focus on the development of more efficient coupling catalysts. Additionally, the solvent exchange from methanol to heptane required for the chain elongation reaction takes a lot of energy and the use of heptane as solvent raises difficulties for further product separation. Therefore, a catalyst that can do the coupling reaction in methanol would be ideal, but how to avoid the participation of methanol in the coupling reaction would prompt a serious challenge.

The LignoFlex process (Chapter 2) resulted in the formation of aromatic alcohol intermediate from lignin and a mixture of aliphatic alcohols from the (hemi)cellulose fraction of lignocellulosic biomass. In our view, the beauty of this approach is that these alcohols are ideally set up for a number of attractive, atom-economic transformations involving the formation of C-C and C-O bonds (Figure 1). This allows that valuable products can be accessed with minimal number of reaction steps and with minimal formation of waste.
Chapters 5 and 6 are focused on the upgrading of the bio-ethanol and other biomass derived primary alcohols with modified Cu-PMO catalysts. Here the research takes advantage of the cation-exchange ability of the Brucite layer of hydrotalcite derived PMO catalysts, which provides a wide versatility in the chemical composition of the obtained structures.

In Chapter 5, several novel compositions of PMOs by doping both copper and nickel were presented as highly active and selective catalysts for the Guerbet reaction of ethanol to 1-butanol. Up to 22% 1-butanol yield at 56% ethanol conversion was reached by doping equimolar amounts of copper and nickel. Recycling and leaching tests showed excellent robustness of the new catalysts. Further test in continuous flow reactor confirmed the good stability of prepared CuNi-PMO catalyst. After 162 hours the conversion of ethanol showed slightly fluctuations at the range of 20% to 30% and the selectivity of 1-butanol was stabilized at around 55%. Structural characterization before and after reaction revealed the formation of metal nanoparticles as well as the existence of a Ni-Cu alloy phase that likely
plays a role in the excellent catalytic performance. However the exact role of Ni-Cu alloy in this reaction is still not clear and more specific characterization experiments like in situ XRD or high resolution TEM would be necessary to explain the formation of this alloy structure. Theoretical calculations could also be extremely useful to explain the synergistic effect of Ni-Cu alloy for Guerbet coupling of ethanol.

In Chapter 6, the possibility of using methanol and other primary alcohols as renewable carbon sources for the construction of the benzimidazoles and N-methylbenzimidazole moiety was presented. In this process, the solvent serves as a source of in situ formed aldehydes, thus useful carbon for the construction of the benzimidazole core through the catalytic acceptorless dehydrogenative condensation strategy. After screening of different dopants, CuZn-PMO was found as the most active among the catalysts tested, and afforded the highest selectivity to benzimidazole. Interestingly, the more challenging, but readily available 2-nitroanilines, which requires an additional reduction step prior to cyclization, could also be successfully converted to benzimidazoles in high selectivity. Significant differences were observed by comparing different catalyst compositions: the performance of Cu-PMO and CuNi-PMO was comparable but considerably lower than the Ru- and Zn-doped PMO catalysts. This new method could be successfully extended to a variety of 1,2-diaminobenzenes and 2-nitroanilines and afforded to the corresponding mixtures of benzimidazoles and N-methylated analogues in good yields. Furthermore, various other primary alcohols were applied besides methanol, to obtain 2-alkyl- and 1,2-dialkylbenzimidazoles. Preliminary mechanistic insights into the origins of N-alkylation as well as the reactivity of the nitro derivatives are also discussed.

The described methodology in Chapter 6 displays a number of advantages compared to other methods: (a) neat alcohol is both solvent and reactant in order to access targeted benzimidazoles or 2-alkylbenzimidazoles, (b) no additives (oxidants, bases or acids) other than the solvent are needed, (c) catalysts consist of readily available, inexpensive metals and (d) only water and hydrogen are generated as by-products. Future efforts should be focused on the synthesis of valuable N- and O-heterocyclic compounds and developing more active dehydrogenation catalysts that can operate at milder reaction conditions. The promoting effects of Zn should be explained by more intensive characterizations.

Chapter 7 described the development of a simple two-step process that aiming to completely convert lignocellulose to alkanes. The first step involved the total conversion of raw lignocellulose to alcohols in supercritical methanol (sc-MeOH) by Cu-PMO and the second step performed the HDO of the produced alcohols to alkanes using a solid acid together with Pd/C as catalysts in dodecane. For the first step, the relationship between catalyst composition and product distributions was investigated and with this goal a deep insight into the compositions of produced alcohol mixtures was performed. For the second step, different solid acids were compared and Nafion and HZSM-5 gave the best synergistic effects on the production of alkanes. Finally, the product mixture from step 1 by
depolymerization of pine lignocellulose could be upgraded to alkanes with around 85% selectivity. This two-step process introduced a new way for converting raw lignocellulose to alkanes; however there are still several challenges for further industry applications. One limitation would be the solvent change from methanol to dodecane required between step 1 and step 2. This process may lead to the loss of some compounds and uses a lot of energy. Some of the produced alkanes have a chain length that is short and are too volatile to be used as fuels and are also hard to be quantified. Finally, Pd/C as a noble metal catalyst would definitely increase the total cost of this process.

In summary, this thesis attempts to give a better understanding of strategies for catalytic valorization of lignocellulose, from process design to catalyst preparation, from depolymerization of complex biopolymers to functionalization of simple molecules. Most attention has been devoted to understanding the current processes in order to design more sustainable processes with low energy input and less waste produced. Although some of the developed processes described in this thesis show great advantages compared with current processes, several key challenges still need to be solved for further applications. The Cu-PMO catalyst is selected as the main catalyst structure in this thesis for its unique properties. Modification of this catalyst gave me a lot of joy and opportunities for learning and understanding each catalytic process described in this work. Lignocellulose, as the main substrate of this thesis, gave me a lot of trouble at the beginning due to the complexity of its structure but also provided a great sense of achievement when finally I found the best way to use it properly. Without any doubt, I believe the exciting developments achieved thus far would bring a bright future for lignocellulose valorization and I hope my work presented in this thesis provides a small contribution to this in the near future.