Title: Noble metals-free heterogeneous catalysts for lignin deoxygenation into aromatics

Proposal summary: The transformation of lignocellulosic biomass into fuels or reaction synthons of interest for fine chemistry is an essential issue for reducing the environmental impact associated with the use of fossil resources. Contrary to cellulose and hemicellulose, lignin is a resource that is still not very well valorized, although it is abundantly produced by the pulp and paper industry and will be an abundant by-product of next generation cellulosic biorefineries. Different technologies exist for lignin liquefaction, but fast pyrolysis has undeniable advantages. It can convert 60-75% of lignocellulosic biomass into crude bio-oil, and it operates continuously, in an inert environment, and without solvent consumption. However, the bio-oil must be upgraded to be valorized. Containing up to 55% of phenolic compounds, it is a source of simple aromatic hydrocarbons (BTX). Catalytic hydrodeoxygenation (HDO) is the most suitable catalytic process to transform phenolic monomers into BTX. The catalyst, by selectively activating the C-O bonds, will allow the deoxygenation of phenolic compounds while avoiding their hydrogenation. These two processes are therefore essential to ensure the economic viability of biorefineries through a better valorization of the lignocellulosic fraction. The project aims developing original catalysts for the deoxygenation of lignin pyrolysis vapors, with the goal to improve the yield of aromatic hydrocarbons. In order to gather skils in materials chemistry, molecular modelling, heterogeneous catalysis and process engineering, the project team associates 5 laboratories, labelled by CNRS: UCCS (Univ. Lille), IC2MP (Univ. Poitiers), and L2CM, LPCT, and LRGP (all three from Univ. Lorraine). The skills thus gathered allow the development of a multi-scale approach, from *ab initio* modeling at the molecular scale of surfaces to the study of catalyst performance on lignin pyrolysis vapors from a continuous hydropyrolysis process.
The PhD project will aim at synthesizing heterogeneous catalysts based on abundant metals, whose key parameters will be optimized: (i) textural properties of the supports, and in particular the stabilization of a hierarchical porosity, (ii) oxophilicity / acidity of the surface, (iii) and fine characteristics of the metals (dispersion, localization and composition). Thus, silica supports with hierarchical porosities will be synthesized, modified by the introduction of different oxide phases (ZrOx, TiOx, AlOx, ZnO), and then the metal phases (Ni, Fe, Co and Cu) will be dispersed in a controlled manner on the surface of the pores to obtain single atome to clustered supported catalysts. These catalysts will be studied for the HDO of model oxygenated molecules (*m*-cresol, anisole and guaiacol) under moderate hydrogen pressures (2-4 MPa) before being tested on real lignin in a reaction micropilot (IC2MP partner). The properties of the catalysts (activity, aromatic yield, and stability) will be rationalized by DFT studies conducted on the adsorption of model oxygenated molecules, taking into account the effect of H_2O, CO and CO_2 inhibitors (LPCT partner). All these results will allow the description of the reaction pathway and the obtaining of key kinetic data in real conditions of reaction conducted over lignin (at LRGP partner).

Starting date: Flexible, until march 2021

Application: CV + motivation letter by email to the supervisors

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Laboratory information:
French partner: http://uccs.univ-lille1.fr/index.php/en/heterogeneous-catalysis/matcat

Salary:
Approx. 1600 euros net/month