ABSTRACT

Ligno-cellulosic biomass from agricultural and forest residues —which does not compete with land use for other crops or for food production— is presented as an alternative to chemicals and fuels production, diminishing our dependence on fossil raw materials. Nowadays, processes for transformation of renewable raw materials (i.e. vegetal biomass) to produce hydrocarbons and other chemical products are more expensive than the conventional petrochemical processes, so that the valorization processes for the biomass and the obtained bio-products are not competitive with their analogs derived from petroleum. For this reason, we think that a major challenge for chemists is to try to develop new catalytic routes to convert biomass and its derivatives into fuels and chemicals through sustainable and economically viable processes.

In this doctoral thesis, solid catalysts and catalytic processes have been developed to carry out different transformations of biomass derivatives by means of consecutive cascade-type reactions (one-pot processes), obtaining high added-value chemical products. The valorization of biomass derivatives studied comprised platform compounds derived from cellulose and hemicellulose rich fractions (i.e. furfural and 2-methyl furan), as well as those derived from lignin-rich fractions (i.e. guaiacol, syringaldehyde, etc.).

Furfural is one of the studied biomass derivatives, and for its transformation into furfuryl and tetrahydro-furfuryl alcohols have been designed selective hydrogenation catalysts based on metal supported on different metal oxides. Particularly, for furfural hydrogenation, high selectivity to furfuryl alcohol was obtained by working with Pt-based catalysts. While excellent yields to tetrahydro-furfuryl alcohol were reached by Ru-based catalysts (i.e. Ru/Al_2O_3 and Ru/ZrO_2). The Ru/ZrO_2 catalyst reached the best results, also that catalyst has displayed great stability during several re-uses, even in aqueous reaction media. Furthermore, it has been indicated that the different ZrO_2 polymorphs exhibit an influence on the catalytic activity of these materials.

Also, have been investigated a one-pot process to obtain furfuryl ethers from furfural by a cascade-type reactions process, which implicate etherification and reduction stages (reductive-etherification). For this process, Pd-based catalysts supported on different metal oxides were developed. The best results were reached by working with Pd/ZrO_2 and Pd/TiO_2 catalysts,

which in combination with alcohols (i.e. butan-1-ol, pentan-1-ol, hexan-1-ol, etc.) were active for the synthesis of furfuryl ethers and tetrahydro-furfuryl ethers, those compounds being an interesting group of fuel additives.

The catalytic transformation of 2-methyl furan —a furfural derivative— by hydrolysis/condensation process to produce intermediate compounds have been also studied. After a hydrogenation process, this kind of compounds yields chemical products with industrial application. Thus, a process that uses an ionic exchange polymeric resin as solid acid catalyst combined with a benign reactive/solvent system (water/ethanol) was developed, this process indicates advantages with respect to previously reported processes that utilize mineral or organic acids as catalysts. In addition, the study includes the proposal of a possible reaction mechanism and a first-order kinetic model for the process, confirming that the hydrolysis of 2-methyl furan is the rate-limiting step of the global process.

Finally, the catalytic transformation of phenolic compounds derived from lignin was studied by mean of a hydrogenation/hydrodeoxygenation (HYD/HDO) process in aqueous phase, catalyzed by materials based on Pd, Pt and Ru supported on different metal oxides. It has been demonstrated that the hydrodeoxygenation capacity of these materials turned out to be dependent on the type of metal and the solid support used. The best yields for hydrodeoxygenation (HDO) products were reached with Ru and Pd catalysts, also resulting active for the upgrading of a fraction of oligomers derived from lignin depolymerization, with good yields to phenolic monomers and C6-C8 alcohols.

Summarizing, the work developed during this thesis shows how through the study of different multifunctional solid catalysts, with specific and controlled properties, and under suitable reaction conditions, catalytic processes can be developed to transform biomass-derived platform compounds in a series of chemical products with diverse and interesting applications.