## Superparamagnetic Core Shell Catalysts for the Environmental Production of Fuels from Renewable Lignin

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Abstract : The tremendous achievements in the development of the society concretized by more sophisticated materials and systems are merely based on non-renewable resources. Consequently, after more than two centuries of intensive development, among others, we are faced with the decrease of the fossil fuel reserves, an increased impact of the greenhouse gases on the environment, and economic effects caused by the fluctuations in oil and mineral resource prices. The use of biomass may solve part of these problems, and recent analyses demonstrated that from the perspective of the reduction of the emissions of carbon dioxide, its valorization may bring important advantages conditioned by the usage of genetic modified fast growing trees or wastes, as primary sources. In this context, the abundance and complex structure of lignin may offer various possibilities of exploitation. However, its transformation in fuels or chemicals supposes a complex chemistry involving the cleavage of C-O and C-C bonds and altering of the functional groups. Chemistry offered various solutions in this sense. However, despite the intense work, there are still many drawbacks limiting the industrial application. Thus, the proposed technologies considered mainly homogeneous catalysts meaning expensive noble metals based systems that are hard to be recovered at the end of the reaction. Also, the reactions were carried out in organic solvents that are not acceptable today from the environmental point of view. To avoid these problems, the concept of this work was to investigate the synthesis of superparamagnetic core shell catalysts for the fragmentation of lignin directly in the aqueous phase. The magnetic nanoparticles were covered with a nanoshell of an oxide (niobia) with a double role: to protect the magnetic nanoparticles and to generate a proper (acidic) catalytic function and, on this composite, cobalt nanoparticles were deposed in order to catalyze the C-C bond splitting. With this purpose, we developed a protocol to prepare multifunctional and magnetic separable nano-composite Co@Nb2O5@Fe3O4 catalysts. We have also established an analytic protocol for the identification and quantification of the fragments resulted from lignin depolymerization in both liquid and solid phase. The fragmentation of various lignins occurred on the prepared materials in high yields and with very good selectivity in the desired fragments. The optimization of the catalyst composition indicated a cobalt loading of 4wt% as optimal. Working at 180 oC and 10 atm H2 this catalyst allowed a conversion of lignin up to 60% leading to a mixture containing over 96% in C20-C28 and C29-C37 fragments that were then completely fragmented to C12-C16 in a second stage. The investigated catalysts were completely recyclable, and no leaching of the elements included in the composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

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