

SOLVENT-BASED CATALYTIC STRATEGIES FOR THE SELECTIVE HYDROGENOLYSIS OF LIGNIN AND SELECTIVE DEFUNCTIONALIZATION OF BIO-OIL UNDER LOW-SEVERITY CONDITIONS

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The conversion of lignin, the most recalcitrant of the biopolymers, is required for a carbon-efficient processing of lignocellulosic materials. In this context, hydrogenolysis of lignin is a process option receiving currently increasing attention. In the first part of this communication, the solvent effects on the performance of Raney Ni in the hydrogenolysis of diphenyl ether will be addressed.¹ The practical implications for the hydrogenolysis of lignin will be also discussed. GCxGC-MS reveals that conducting the hydrogenolysis of lignin in methylcyclohexane results mainly in saturated products (e.g., cyclic alcohols and cyclic alkanes), whereas performing the reaction in 2-propanol leads to a very complex mixture of saturated and unsaturated products (e.g., cyclic alcohols, cyclic ketones and hydrocarbons). In turn, when carried out in methanol, the hydrogenolysis of lignin leads to phenols.

In the second part of this communication, the fundamental chemical aspects of hydrogen transfer reactions with Raney Ni and 2-propanol in the defunctionalization and hydrodeoxygenation of phenolic and aromatic biorefinery feeds under low-severity conditions will be addressed.² A series of 32 model substrates were explored, providing a comprehensive description of the reactivity of Raney Ni toward transfer hydrogenation and transfer hydrogenolysis of phenolic and aromatic compounds. With regard to the processing of a model-substrate mixture, important features of the chemoselectivity of Raney Ni were also revealed. Hydrogen transfer reactions could hold the key for the upgrade of bio-oil under unusual, low-severity conditions. In fact, bio-oil was easily upgraded to cyclohexanols and less functionalized alkylphenols, with Raney Ni and 2-propanol, already at 120 °C. Full saturation of bio-oil to cyclic alcohols, cyclohexane-1,2-diols and other products with reduced oxygen content was achieved at 160 °C under autogenous pressure.

REFERENCES

1. X. Wang, R. Rinaldi, Solvent effects on the hydrogenolysis of diphenyl ether with Raney Nickel and their implications for the conversion of lignin, *ChemSusChem* 5 (2012) 1455-1466.
2. X. Wang, R. Rinaldi, Exploiting H-transfer reactions with Raney Ni for upgrade of phenolic and aromatic biorefinery feeds under unusual, low-severity conditions. *Energy & Environmental Science*, 5 (2012) 8244-8260.