

## Poster session 2 - Green Chemistry

P-0658

**ONE-POT SYNTHESIS OF PARACETAMOL VIA THE CATALYTIC REDUCTIVE CARBONYLATION OF p-NITROBENZENE IN ACETIC ACID-WATER AS A SOLVENT****A. VAVASORI<sup>1</sup>, M. CAPPONI<sup>1</sup>, L. RONCHIN<sup>1</sup>**<sup>1</sup> *Universita Ca' Foscari, Molecular Sciences and Nanosystems, Venezia, Italy*

Paracetamol (N-(4-hydroxyphenyl)acetamide) is a major ingredient in numerous cold and flu medications due to its analgesic and antipyretic properties. A number of commercial methods of paracetamol manufacture are currently in use around the world. Some commonly used processes start from chlorobenzene, phenol or nitrobenzene. All the industrial processes actually used, however, show several drawbacks. For instance, they are based on multistep routes which sometimes lead to poor overall yield, or show serious effluent problems. The increasingly stringent environmental legislation has generated a pressing need for cleaner methods of chemical production, for instance introducing technologies that reduce or, preferably, eliminate the generation of waste and avoid the use of toxic and/or hazardous reagents and solvents. According with this, we propose a new approach for the synthesis of paracetamol: by using Pd(II)-diphosphine catalyst precursors, in acetic acid-water as a solvent, we obtain paracetamol with high selectivity from nitrobenzene in one-pot. At 140 °C and under 45 atm of CO, p-nitrobenzene is completely converted to paracetamol and N-phenylacetamide. The latter is the major by-product of the reaction (ca. 15 molar %, under such reaction conditions) and also an interesting target for the pharmaceutical industry. The selectivity is influenced by several variables such as solvent composition (H<sub>2</sub>O-acetic acid ratio), temperature and batch time. The high temperature and the increase of reaction time favor the acetylation reaction, which occurs in-situ when p-aminophenol and aniline readily form from nitrobenzene/CO/H<sub>2</sub>O. Such reaction is proposed as a new sustainable alternative to the synthesis of paracetamol. The absence of chlorobenzene (chlorine-free chemistry), the use of efficient catalysts and the possibility to realize a single step process, make this reaction interesting to be evaluated as a possible alternative to the multi-steps industrial processes actually used.

**Keywords:** Carbonylation; Reduction; Homogeneous catalysis; Sustainable Chemistry;

P-0659

**CATALYTIC DEPOLYMERIZATION OF LIGNIN UNDER ULTRASOUNDS CONDITIONS****M. VERZIU<sup>1</sup>, A. RICHEL<sup>2</sup>, R.M. RICHARDS<sup>3</sup>, V.I. PARVULESCU<sup>1</sup>**<sup>1</sup> *University of Bucharest Faculty of Chemistry, Department of Organic Chemistry Biochemistry and Catalysis, Bucharest, Romania*<sup>2</sup> *University of Liege – Gembloux Agro-Bio Tech, Unit of Biological and Industrial Chemistry, Gembloux, Belgium*<sup>3</sup> *Colorado School of Mines, Department of Chemistry and Geochemistry, Golden, USA*

Lignin is an aromatic polymer including three main phenylpropane units, namely *p*-coumaril, coniferyl and sinapyl alcohol which are linked by C-C or C-O-C. Recently Lavoie et al have reported depolymerisation of lignin in the presence of NaOH[1]. However, using homogenous catalysts is necessary a purification step of the reactions products that is a non-friendly environmental process producing high amounts of waste waters. A solution to this problem can be the use of heterogeneous catalysts because they can be recovered at the end of the reaction by centrifugation providing green, recyclable catalytic systems.

In this study we investigated the influence of the crystallographic phase of Ru (RuNi, RuNiO and Ru/Al<sub>2</sub>O<sub>3</sub>) in conversion of lignin to low molecular weight compounds under ultrasounds conditions. RuNi and RuNiO were prepared by replacement reaction between nickel or nickel oxide and RuCl<sub>3</sub> in aqueous solution[2] while Ru/Al<sub>2</sub>O<sub>3</sub> was prepared by wet impregnation of mesoporous alumina with a RuCl<sub>3</sub> aqueous solution. These materials were characterized by several techniques like: XRD, BET, XPS, etc. Lignin tested in this study was extracted from miscanthus plants under both acid and basic conditions[3] and was characterised by DRIFT and TGA/DTA. Depolymerisation of lignin was carried out under bubbling hydrogen in special designed ultrasound reactor. The reaction products analyzed by LC-MS had molecular weights with m/z below 1000 g/mol, that confirmed the depolymerization of lignin. Among the investigated catalysts RuNi led to an advanced depolymerisation of lignin.

**Acknowledgement:** "This work was supported by the strategic grant PO SDRU/89/1.5/S/58852, Project 'Postdoctoral programme for training scientific researchers' co-financed by the European Social Foundation within the Sectorial Operational Program Human Resources Development 2007–2013"

**References:**

1. Lavoie J.M., Baré W., Bilodeau M., Bioresource Technology 102 (2011) 4917.
2. Zhao Z.F., Wu Z.J., Zhou L.X., Zhang M.H., Li W., Tao K.Y., Catalysis Communications 9 (2008) 2191.
3. Vanderghem C., Richel A., Jacquet N., Blecker C., Paquot M., Polymer Degradation and Stability doi:10.1016/j.polymdegradstab.2011.07.022.

**Keywords:** lignin; ultrasounds; heterogeneous catalysts;

