RUTHENIUM IMMOBILIZED ON A MAGNETICALLY RECOVERABLE SOLID: A HETEROGENIZED CATALYST FOR LIQUID-PHASE HYDROGENATIONS AND OXIDATIONS

L.M. Rossi[1], M.J. Jacinto[1], O.H.C.F. Santos[1], R.F. Jardim[2]

1 - University of Sao Paulo, Institute of Chemistry, Sao Paulo, Brazil

2 - University of Sao Paulo, Institute of Physics, Sao Paulo, Brazil

lrossi@iq.usp.br

A green oxidation or reduction process should involve a highly active and selective recyclable catalyst that is able to work under mild conditions (pressure and temperature) using environmentally-benign molecular oxygen or hydrogen, as oxidant and reductor, in the absence of solvents and other aditives. However, stoichiometric oxidations using transition metal compounds such as chromium(VI) and manganese compounds or reductions using $NaBH_4$ and $LiAlH_4$ are still commonly used, despite the formation of large amounts of toxic waste. For instance, several homogeneous catalysts are able to perform oxidations reactions, although the product recovery and catalyst recycling are problematic. Increasing separability of catalysts, maintaining the high activity and selectivity, is a challenging research area in Green Chemistry. Here we present our results on the immobilization of ruthenium on a magnetically recoverable support in order to obtain a recyclable catalyst for hydrogenation and oxidation reactions. Magnetic separation has been suggested as a very promising technique to improve recovery of metal-based catalysts in liquid-phase reactions [1]. The separation method is significantly simple as it does not require filtration, decantation, centrifugation, or any other separation technique thereby, overcoming traditional time- and solvent-consuming procedures.

The magnetically recoverable Ru catalyst was prepared by coordination of Ru(III) to NH_2-modified silica coated magnetic nanoparticles. The resulting nanocatalyst converts various alcohols to the corresponding aldehydes and ketones catalyst and was easily recovered with a permanent magnet on the reactor wall after each experiment. Under reducing conditions of H_2, the metal is reduced leading to the formation of Ru(0) nanoparticles on the magnetic support surface. The catalytic

activity of the magnetically separable Ru(0) catalyst was investigated in the hydrogenation of cyclohexene and benzene in solventless conditions. Turnover frequencies (TOF) as high as 6700 and 1000 h^{-1} were obtained in the hydrogenation of cyclohexene and benzene at 75ºC and 6 atm H_2. In conclusion, the ruthenium catalyst can be easily separated magnetically from the reaction products of oxidations and hydrogenation reactions, which can reduce the environmental impact of the processes. This work was supported by FAPESP and CNPq. We also thank LNLS for catalysts characterization by HRTEM.

Literature: [1] T.-J. Yoon, W. Lee, T.-S. Oh, J. K. Lee *New J. Chem.* **2003**, *27*, 227. P. D. Stevens, G. Li, J. Fan, M. Yen, Y. Gao *Chem. Commun.* **2005**, 4435. A. Hu, G. T. Yee, W. Lin *J. Am. Chem. Soc.* **2005**, *127*, 12486. Kotani, M.; Koike, T.; Yamaguchi, K.; Mizuno. N. *Green Chem.* **2006**, *8*, 735. Zheng, Y.; Stevens, P. D.; Gao, Y. *J. Org. Chem.* **2006**, *71*, 537. Rossi, L. M.; Silva, F. P.; Vono, L. L. R.; Kiyohara, P. K.; Duarte, E. L.; Itri, R.; Landers, R.; Machado, G. *Green Chem.*, **2007**, *9*, 379.