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Denise Cavuoto

Titolo Tesi di Dottorato

Green strategies for the synthesis of biobased building-blocks

Corso di Dottorato

Chimica Industriale

Tutor

Prof. Antonella Gervasini

Università degli studi di Milano, Dipartimento di Chimica

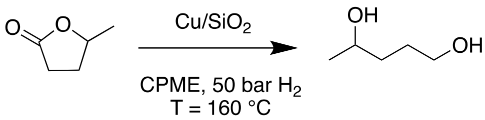
Co-tutor

Dr.ssa Federica Zaccheria

Consiglio Nazionale delle Ricerche, Istituto SCITEC

Sintesi della Tesi

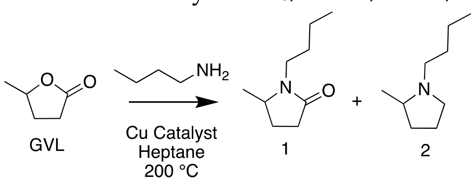
Green chemistry is an important tool in the roadmap towards a circular economy system. Biomass-waste valorization, in particular ligno-cellulosic wastes, and the use of sustainable processes are pillars of the green chemistry approach [1]. In particular, biobased lactones can be valorized towards new valuable molecules such as diols and amines that are ubiquitous chemicals in today's chemical industry. The use of available and cheap supported heterogeneous copper catalysts, prepared with the Chemisorption-Hydrolysis method [2], will avoid toxic and expensive noble metal catalysts. The first part of the Ph.D project was devoted to study the hydrogenation of γ-valerolactone (GVL) to 1,4-pentanediol (1,4-PDO) (Scheme 1), using silica supported copper catalysts under a green solvent such as Cyclopentyl Methyl Ether (CPME).



Scheme 1: Hydrogenation of GVL to give 1,4-PDO.

Deep characterization was performed on the catalytic system to enlighten the relationship between physicochemical properties of the catalysts with the performances. The activity was found to depend on SiO_2 support wettability and on the nature and *effective* number of the acid sites on the surface. The use of CPME, that modulates the acidity, and of a less hydrophilic silica allowed to reach 78% yield in 1,4-PDO. After this, a series of Cu/SiO_2 trietoxyoctylsilane-grafted systems with gradually reduced hydrophilicity has been prepared and used in the same hydrogenation reaction. The surface modification obtained with the proposed procedure allows to significantly increase the selectivity (99%) of the process and therefore the yield in the desired diol.

The second part was focused on the synthesis of N-heterocycles always starting from GVL that can be used as benign alternative solvent or as the starting material for the synthesis of agrochemicals and pharmaceuticals [3]. GVL has been coupled with butylamine to obtain N-butyl-5-methyl-2-pyrrolidone (1) and N-butyl-5-methyl-2-pyrrolidine (2) (Scheme 2) utilizing similar supported copper catalysts on different materials namely Al_2O_3, ZrO_2, TiO_2, hydroxyapatite (HAP), SiO_2 and SiO_2-Al_2O_3.



Scheme2 : Reaction of lactamization of GVL.

The reaction conditions and set up were improved lower the impact avoiding any catalyst pre-treatment and high hydrogen pressure. The system has showed its efficacy for the lactamization of other biobased lactones. Moreover, the activity and selectivity can be easily tuned by varying the acidic properties of the support.

References

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3. Gao, F.; Bai, R.; Ferlin, F.; Vaccaro, L.; Li, M.; Gu, Y. Replacement strategies for non-green dipolar aprotic solvents. *Green Chem.* **2020**, *22*, 6240–6257.