Università degli Studi di Salerno

Dipartimento di Chimica e Biologia "Adolfo Zambelli"

PhD Course in Chemistry

XXXI Cycle

CATALYSIS FOR THE TRANSFORMATION OF BIOMASS IN VALUE-ADDED PRODUCTS

PhD Student: *Maria Ricciardi*

Supervisor: *Prof. Antonio Proto*

Co-Supervisor: *Prof. Carmine Capacchione*

External Supervisor: *Prof. Fabrizio Passarini*

PhD Course Coordinator: *Prof. Gaetano Guerra*

Academic year 2017-2018

Abstract

The present doctoral thesis is focused on the catalytic conversion of bio-glycidol into value-added products.

Bio-glycidol (2,3-epoxy-1-propanol) is obtained from 2-chloro-1,3-propanediol, produced as waste during the Epicerol® process, that represents one of the most consolidated bio-based industrial process able to convert glycerol into epichlorohydrin.

Glycidol, in turn, is successfully employed as starting material to produce glyceryl ethers, propanediols and glycerol ketals.

Homogeneous and heterogeneous Lewis and Brønsted acids were used as catalysts for the etherification of glycidol by ring opening reaction with an alcohol as nucleophile.

As a matter of fact, commercial metal salts (chlorides and triflates of Fe, Al, Bi and Zn) were tested as homogeneous catalysts giving promising results in term of the catalytic activity in the case of metal triflates.

Moreover, a Fe(III) triflate complex bearing and [OSSO]-type ligand was synthesized and used as catalyst to enhance the regioselectivity of the reaction.

Moving to heterogeneous catalysts, sulfonated resins, metal triflates and sulfonic groups supported catalysts were employed in the synthesis of glycerol monoethers, achieving good results.

The proposed synthetic route can be applied to several alcoholic substrates ranging from short chain to long chain alcohols, obtaining precious compounds in high yield.

Considering the hydrogenolysis reaction of glycidol, instead, a system formed by the combination of Amberlyst 15 and palladium on carbon was used as catalyst. An acid resin such as Amberlyst 15 can act as co-catalyst in the hydrogenolysis thanks to its property to activate the epoxide ring

towards the ring opening reaction. The amount of this resin and the solvent medium were optimized in order to reach total selectivity towards 1,2-propanediol.

Lastly, several acid heterogeneous catalysts, both commercially available and synthetic, were tested in the ketalization reaction of glycidol with acetone, producing solketal under mild reaction conditions.

The best catalytic system, under optimized conditions, was selected for the production of other glycerol ketals using different ketones as starting material.

Furthermore, life cycle assessment (LCA) analyses, performed in collaboration with Doctor Daniele Cespi and Professor Fabrizio Passarini, were used as a tool to evaluate the environmental sustainability of the proposed synthetic processes, comparing them with those reported in literature.