University of Salerno - Department of Chemistry and Biology "Adolfo Zambelli"
PhD Doctoral Course in Chemistry - XIV Cycle

Sustainable Catalysis by Polymer Supported Gold Nanoparticles

Abstract

Gold Nanoparticles are nanomaterials whose properties are completely different from the ones of the bulk material. Nowadays many chemists have been using them as catalysts which work under mild conditions and respect the principles *green* and *sustainable* chemistry. The increasing need for new heterogeneous catalysts to be applied in industrial processes encourages the finding of efficient and selective catalytic systems.

The aim of the current PhD project is the synthesis of gold nanoparticles (AuNPs) supported onto a porous polymer matrix, consisting of syndiotactic polystyrene-*co*-cis-1,4-polybutadiene (sPSB) and the use of this hybrid material in redox reactions.

Aerobic oxidative esterification of cinnamyl alcohol and nitroarenes reduction to amines were chosen as benchmark reactions to assess the activity and selectivity of the AuNPs-sPSB catalyst.

In cinnamyl alcohol oxidation and esterification, a large number of products can be obtained, coming from oxidation, dehydrogenation or reduction pathways, but the catalytic system here presented resulted highly selective towards cinnamaldehyde and alkyl cinnamates. The synthetic protocol was successfully extended to *p*-substituted cinnamyl alcohols, and information about the effects of Electron Withdrawing or Electron Donating Groups on the esterification of cinnamyl alcohol were achieved.

Nitroarenes reduction to aniline derivatives is a complex multistep reaction, since the main intermediates are azoxybenzene and azobenzene. Once again, the AuNPs-sPSB catalyst was selective in the aniline formation. Different reaction pathways have been proposed for this reaction; under the reaction conditions here used the *condensation route* proposed by Haber was detected.

The access of reagents to the catalytic active site is facilitated by the presence of nanoporous polymeric matrix, whose role is to determine which species are able to permeate the polymeric matrix in order to reach the AuNPs. Different kinetic studies confirmed this initial hypothesis.

In addition to the AuNPs-sPSB catalyst, gold colloids were immobilized on a polymeric support in order to investigate a different synthetic approach for the achievement of gold nanoparticles. Different supports have been tested, *e.g.* polyvinyl alcohol, polyvinylpyrrolidone, cetrimonium bromide and P123 (a poloxamer triblock *co*-polymer). The removal of the colloid stabilizer was evaluated through catalytic tests.

PhD Student
Dr. Annarita Noschese
Matr. 8880700202

Supervisor
Prof. Alfonso Grassi

Co-Supervisor
Dr. Jose A. Lopez-Sanchez
(University of Liverpool)