
DOCTORAL THESIS

Laboratoire Hétérochimie Fondamentale et Appliquée,
CNRS / Université Toulouse 3 – Paul Sabatier
SYMAC team, <http://symac.lhfa.fr>



Photoactivated dehydrogenations using plasmonic metal nanocomposite catalysts (PLASMOCAT)

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dehydrogenation reactions, photo-chemical processes, mechanistic studies

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Subject

In the current societal context facing high energy prices and resource shortages together with high pollution, catalysis using sunlight as energy source is a promising way to develop innovative sustainable processes for industrial implementations as proven by different approaches described in the literature. **PLASMOCAT** focuses on visible-light mediated dehydrogenation processes under oxidant-free conditions, from low to high challenging substrates (alcohols – amines – alkanes), to provide both feedstock (carbonyl derivatives, imines, nitriles, alkenes) and molecular hydrogen, a carbon-neutral fuel. Also, **PLASMOCAT** foresees to couple the dehydrogenation of alcohols to the decarbonylation of aldehydes as a tandem process, with the aim of obtaining alkanes, including long carbon chain hydrocarbons.

Although photocatalytic dehydrogenation of alcohols has been achieved with nanoparticles (NPs) of Pt, Au or Ag on TiO₂, the employment of zero-valent NPs of 3d transition metals is almost unexplored. Therefore, composite materials combining photo-activation sites and catalytically active sites will be studied. *In particular, the synthesis of original plasmonic NPs of Cu and Co immobilized on different semiconductors, metallic and non-metallic ones, will be developed. Understanding the mechanisms of photocatalyzed dehydrogenation will be crucial for the design of catalytic systems with improved activity and selectivity.* Accordingly, operando techniques (React-IR, UV-Vis, advanced X-ray techniques) will be used to determine the kinetic reaction profiles and elucidate the interactions between the metallic NPs and the support.

PLASMOCAT provides an excellent frame to train young researchers in innovative and sustainable nanocatalytic processes, leading to the synthesis of added value products, including the production of hydrogen. This project will be developed in the frame of a collaborative project funded by the ANR, constituted of two partners, LHFA in Toulouse responsible of the experimental

work and ITODYS in Paris, in charge of the theoretical studies, with the aim of understanding the plasmonic behavior of metallic NPs and the electronic transfer phenomena. This framework will offer the candidate a multidisciplinary environment, actively participating in the meetings and activities planned during the three-year PhD thesis.

Context

The LHFA (www.lhfa.fr) is a joint laboratory of the National Center for Scientific Research and the University Toulouse 3 - Paul Sabatier (UMR 5069) in Toulouse (France), constituted by 5 research teams (16 researchers and professors, 9 technical engineers and administrative staff; ca. 40 doctoral students, post-docs and master students per year). Research activities focus on molecular chemistry of p-block elements of, with transversal actions in the fields of organometallic chemistry, metallic nanoparticles, catalysis and polymers, including mechanistic studies. The SYMAC research team, led by M. Gómez works on the design of metal-based (nano)catalysts for innovative processes, is interested in the application of catalytic materials in synthesis, involving a wide range of transformations, in particular one-pot multi-step processes (sequential/tandem processes). In the last years, we have developed sustainable catalytic processes based on the immobilization of catalytic phases both in liquid media (ionic liquids, glycerol) as well as original functionalized supports serving as stabilizing agents of the metal nanoparticles and facilitating catalyst recycling. Understanding the observed reactivity is at the heart of our research, leading us to in-depth mechanistic studies through reaction monitoring using different techniques (ReactIR, NMR, EPR, SAXS).

The LHFA offers a very dynamic and international framework (ca. 40% of foreign students), with cutting-edge research. The different teams have (inter)national collaborations, both academic and with industrial partners. The LHFA takes part in the organization of (inter)national conferences as well as Summer Schools, and it is involved in various dissemination activities.

Application

Motivated students have the opportunity to join the research group "Metallic Systems Applied in Catalysis" (SYMAC) at the Laboratory of Fundamental and Applied Heterochemistry (LHFA), Joint Research Unit of the CNRS and the University Toulouse 3 - Paul Sabatier.

This doctoral program is aimed at highly qualified students with an enthusiastic interest in the design and development of sustainable processes, including fundamental studies and going as far as applications. Students must have solid knowledge in organic and inorganic chemistry, with a knowledge of spectroscopic techniques; acquaintance of materials chemistry will be appreciated. Requests must include a cover letter, a detailed Curriculum Vitae and the contact of at least one contact person.

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